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Cyanide Removal from Refinery Wastewater Using Powdered Activated Carbon

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The objective of this project was to evaluate the removal of low level cyanide in petroleum refinery wastewater by the addition of powdered activated carbon and cupric chloride to an activated sludge unit. The activated carbon and cupric chloride act as catalyst in the oxidation and destruction of the cyanides.

A two-phase study was carried out to develop the process. The first phase consisted of a bench-scale study using solutions of metal-cyanide complexes in order to determine the mechanics of cyanide destruction. The second phase consisted of bench-scale tests using actual refinery wastes.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation'a land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized. EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

Various effluent standards typically require that cyanide levels be kept below concentrations in the microgram-per-liter range. Such levels are difficult to achieve in industrial operations like petroleum refining because of daily and seasonal fluctuations in raw waste content. This report contains data on a promising treatment technology for effecting significant cyanide reductions with minimal capital investment. Development of such technology is essential if EPA is to establish and enforce pollution control standards which are reasonable, cost-effective, and which provide protection for the American public.

William C. Galegar

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ABSTRACT

This research program was initiated to investigate the feasibility of utilizing powdered activated carbon (PAC) and cupric chloride ($CuCl_2$) for removal of cyanide in refinery wastewaters.

A two-phase program, consisting of batch tests and continuous tests, was conducted to determine the basic chemistry and cyanide removal efficiency of the adsorption and catalytic oxidation of cyanide by PAC, and $CuCl_2$. In the first phase the operating variables of pH, copper dosage, mode of copper addition, carbon dosage, and type of carbon were investigated. The results indicated a pH near neutral (pH 6-8.5) was desirable to obtain low equilibrium cyanide in the aqueous phase while maintaining a low copper level. Cyanide removal, greater than 95%, was readily achieved in the batch tests using 250 mg/ℓ of powdered carbon and 1.0 to 1.5 mg/ℓ of copper on solutions containing 0.5 mg/ℓ iron cyanide. The most important factors in cyanide removal were the copper concentration and carbon concentration in the solution.

Phase II was a series of continuous tests using two laboratory scale activated sludge units and actual refinery wastewater. Both carbon and copper were added to the aeration basin, and the organic removal as well as cyanide removal performance was monitored. The results of these continuous tests revealed that cyanide can be successfully removed through the addition of PAC and $CuCl_2$ into an activated sludge unit. The biological efficiency did not indicate any detrimental effects from the copper addition (with the exception of the first test where the aeration basin was slug-dosed). More carbon is required than predicted in the batch tests due to the organics competing with cyanide for the active sites on the carbon.

An economic evaluation indicated that this process requires little or no capital expenditure and should provide many refineries with an economic approach for reducing effluent cyanide concentrations.

This program was made possible by the co-sponsorship of the U.S. Environmental Protection Agency and the Illinois Institute for Environmental Quality. This report covers a period from September, 1975 to February, 1977, and the actual laboratory studies were completed in July, 1976.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

API -- American Petroleum Institute
BOD -- biochemical oxygen demand
COD -- chemical oxygen demand
GAC -- granular activated carbon
GPM -- gallons per minute
MGD -- million gallons per day
mg/ℓ -- milligrams per liter
ML -- mixed liquor
MLSS -- mixed liquor suspended solids
PAC -- powdered activated carbon
PPM -- parts per million
R^2 -- coefficient of determination for linear regression
SS -- suspended solids
TOC -- total organic carbon
TSS -- total suspended solids

SYMBOLS

CN^- -- cyanide
$CuCl_2$ -- cupric chloride
H_2S -- hydrogen sulfide
$E(M_D)$ -- expected difference in population means
est M_D -- unbiased standard deviation of M_D
M_D -- mean difference
$n-1$ -- degrees of freedom
n -- sample size
s -- standard deviation
t -- 't' statistic with n-1 degrees of freedom
Y_i -- observed value of the i th sample

SECTION 1

INTRODUCTION

The operation of nearly all modern petroleum refineries results in the discharge of cyanides to the receiving streams. The concentration of refineries and other cyanide discharging industries along selected waterways compounds the potential toxic effects in certain waterways. Various cyanide water quality standards from 0.005 mg/ℓ to 0.2 mg/ℓ have been proposed or adopted by state and federal agencies. A few state agencies have also adopted effluent standards of 0.025 and 0.05 mg/ℓ total cyanide to assist in maintaining water quality.

The formation of cyanide in an inherent result in the production of gasoline components where the catalytic cracking process is employed. The cyanide produced in the cracking process ends up in the "sour water" system which is sent to a steam or natural gas stripping column. Some of the cyanide is removed in the stripper, while the remaining cyanide wastewater is eventually discharged to the sewer. Effluent cyanide levels from 0.020 mg/ℓ to 0.2 mg/ℓ are typical in the industry. Large fluctuations, both in the daily and seasonal cyanide levels, makes control of the problem that much more difficult.

Other than the stripping operation and maximizing water reuse, only minimal cyanide treatment is presently practiced in the refining industry. Existing treatment methods for cyanide are characterized by energy-intensive and expensive processes. A potential low-cost cyanide treatment method for petroleum refinery wastewaters was evaluated in this study. The method investigated can be classified as an adsorption/oxidation process and utilizes powdered activated carbon, copper salts, and dissolved oxygen. The potential application point selected for this study was the biological activated sludge units common in the refining industry for secondary wastewater treatment. Utilization of the activated sludge units minimizes the capital investment requirements and also provides biological regeneration of the carbon, thus minimizing the operating expenses.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

1. In the absence of dissolved organic material, inlet cyanide concentrations of 0.5 mg/ℓ can be reduced to below 0.025 mg/ℓ with the addition of powdered activated carbon (PAC), cupric chloride ($CuCl_2$), and dissolved oxygen.

2. The presence of cupric ions in solution greatly enhances cyanide adsorption. As demonstrated in the batch tests, overall cyanide removal increased from 65% to 99% when the copper level was raised from 0.5 mg/ℓ to 1.5 mg/ℓ.

3. The cyanide level in refinery effluents can be reduced from current levels through the use of PAC and $CuCl_2$.

4. For most refineries the most economical location of a PAC/$CuCl_2$ process is the refinery wastewater activated sludge units.

5. When there is a high organic loading in the wastewater, competition for the adsorption sites occurs between the organics and the cyanide. As the organic quantity increases, the amount of carbon required becomes greater. The most economically favorable location for a PAC/$CuCl_2$ system is the second stage of a biological system or in a stream of low organic loading.

6. The economics of PAC/$CuCl_2$ systems vary according to refinery flow, cyanide level, and organic loading. For example, the costs estimated for four refineries with single-stage activated sludge units range from $46,000 to $500,000 per year. The location of this cyanide removal process in the second stage of an activated sludge unit could reduce the costs to $20,000 to $150,000 per year for the same refineries. Clearly, the second stage, where available, is a more economical location for the PAC/$CuCl_2$ process.

7. For refineries that currently employ the activated sludge process, little or no capital expenditure is required to use PAC/$CuCl_2$ for cyanide removal. Thus the flexibility of this process is enhanced. PAC/$CuCl_2$ can be used for short term cyanide peaks in the effluent attributed to refinery turnarounds or operating changes in the catalytic cracking unit.

8. The experimental results indicate that cyanide removal is possible with a PAC/$CuCl_2$ process; however, the effectiveness of long term treatment is uncertain at this time. The effect of fluctuating organic loadings and the stability of the treatment system over an extended time period need to be better defined for satisfactory application of this process. Sufficient

data have been gathered to develop a full scale study in a refinery for delineation of PAC's operational feasibility. Especially since no capital investment is required, the success of the PAC/$CuCl_2$ process as a practical tool for refineries can be readily demonstrated and should be considered as an important sequel to this study.

SECTION 3

BACKGROUND

Before presenting the results from this study, background information related to the cyanide problem is provided. In this section a description of the source of cyanide in refineries and existing state and federal laws is included, along with the potential advantages and limitations of the proposed treatment scheme. This background material delineates the need for an economical cyanide treatment method and the potential of the treatment scheme is investigated in this study.

CYANIDE GENERATION IN PETROLEUM REFINERIES

Cyanides are present in the effluents of nearly all modern petroleum refineries in the United States. The principal source of cyanide in a refinery is the catalytic cracking unit, with some contribution from the coking unit. Over 92% of the U.S. refineries utilize the cracking process to break heavy petroleum fractions into principally gasoline components. Two types of cracking units are common in the industry, thermal and catalytic. As the name implies, thermal cracking requires high temperatures (900-1100°F) and high pressures (600-1000 psig) to break down the heavy petroleum fractions. Catalytic cracking requires lower temperatures and pressures. The most common catalytic process is the fluid catalytic cracker (FCC) unit, which contains a powdered catalyst.

The trend during the last decade has been toward larger fluid catalytic cracking units because of the higher gasoline yields produced. Over 57% of the refineries in the United States use a catalytic cracking unit to meet the high demand for gasoline (relative to fuel oils). Cyanide is a major pollutant in the wastewaters from refineries employing cracking units, especially the catalytic cracking units.

Presented in Figure 1, is the path the cyanide waste stream follows in a "typical" refinery. As the heavy feedstocks are cracked in the reactor section, many different compounds are formed. A large amount of nitrogen is liberated in the form of ammonia; however, what appears to be a small amount of cyanide is also generated, typically 5 to 100 ppm. From the reactor chamber, all cracked material goes overhead as a gas to a distillation column, where the cyanide and ammonia are distilled off the top of the column with lower molecular weight organics, (butane and lighter). Because of the extremely corrosive nature of the cyanide gas, water is injected in the overhead gas line from the fractionating column. This water is collected in one or two accumulators or knockout drums.

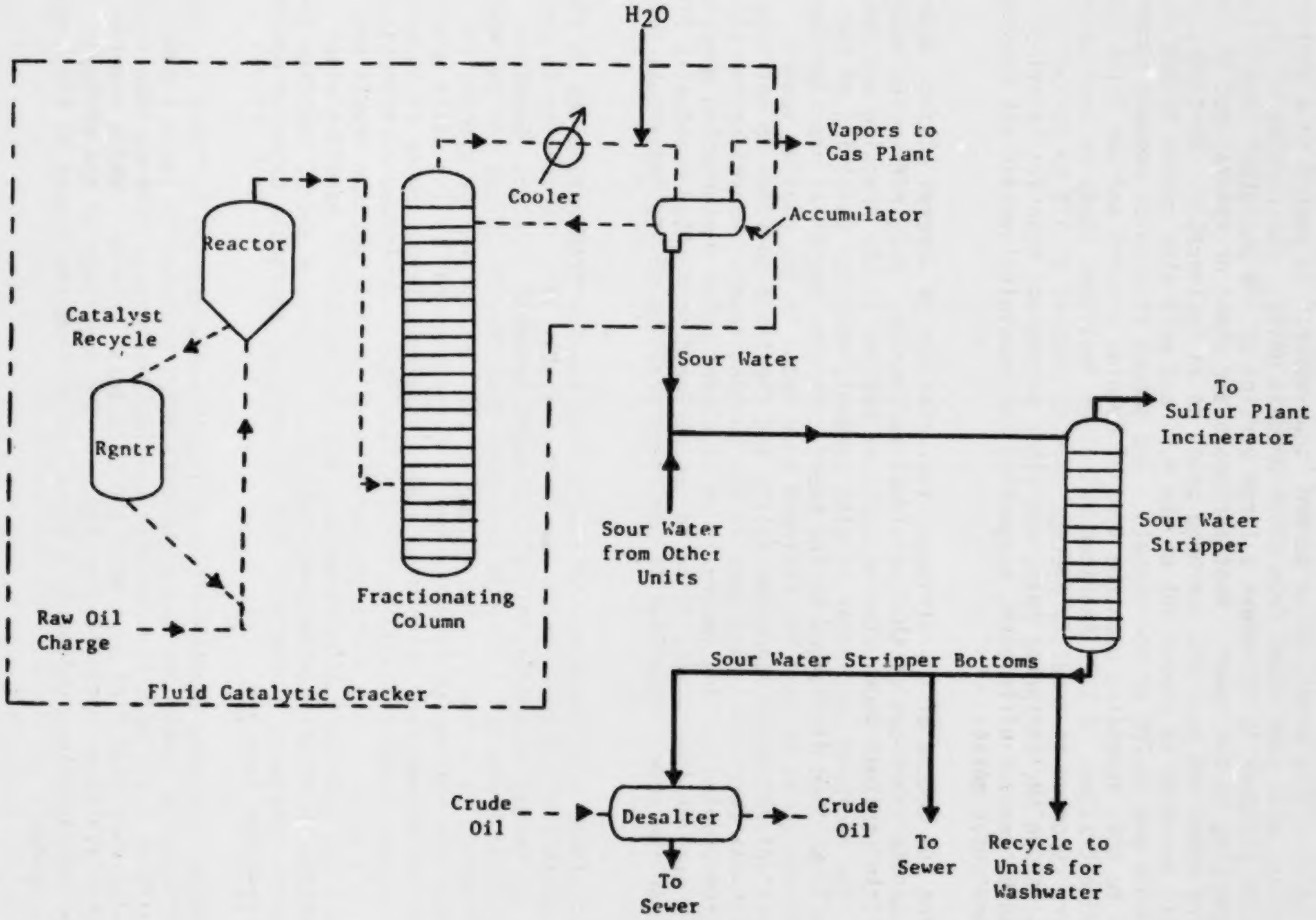

H2O
Vapors to Gas Plant
Cooler
Accumulator
Reactor
Catalyst Recycle
Rgntr
Raw Oil Charge
Fractionating Column
Fluid Catalytic Cracker
Sour Water
Sour Water from Other Units
To Sulfur Plant Incinerator
Sour Water Stripper
Sour Water Stripper Bottoms
Crude Oil
Desalter
Crude Oil
To Sewer
To Sewer
Recycle to Units for Washwater

Figure 1. Cyanide generation and disposal in refinery.

The accumulator water contains high levels of cyanide (20-200 mg/ℓ), phenols (500-2000 mg/ℓ), sulfides (1,000-10,000 mg/ℓ), and ammonia (1,000-10,000 mg/ℓ). This water, often termed "sour-water," is pumped to a stripping column along with sour water from other process units. The purpose of the sour water stripper is to remove a large portion of the pollutant load prior to discharging to the sewer. Most strippers use steam or natural gas as the stripping agent and send the overhead gases to an incinerator. Strippers are typically designed to remove 99% of the H_2S, and will also remove 90-98% of the ammonia and 30-70% of the phenols. The amount of cyanide removed ranges from 20 to 80%, depending upon the type of cyanide present and the inlet cyanide concentration. A 1972 American Petroleum Institute study on sour water strippers reported an industry average cyanide removal of 37% by stripping.[1] Changes in the pH, stripping rate, and other variables, have little effect on the cyanide removal efficiency, suggesting the remaining cyanide has complexed with some heavy metals.

From the bottom of the stripper, the water can go several places, depending upon the practices of the individual refineries. Many refineries return part of the stripped sour water or stripper bottoms to the cracking and coker units. The stripped sour water is also commonly used for desalting of the crude oil and then discharged to the sewer. Another potential practice for some refineries is to send the stripped sour water to the cooling towers. Where reliable stripper operation exists and the trace sulfides do not interfere with the corrosion inhibitors in the cooling towers, recycling the stripper bottoms to the cooling towers is an excellent water conservation practice. However, most of the cyanide found in the stripped sour water eventually finds its way to the sewer regardless of the reuse practice of the individual refineries.

One of the major problems in controlling cyanide from refineries is the large variability in the cyanide levels generated. This variability is not only a day-to-day phenomena, but also a month-to-month problem. Shown in Figures 2 and 3 are daily cyanide frequency distribution curves for two modern refineries in Illinois. The change in the monthly average cyanide for these same two refineries is presented in Figures 4 and 5. The daily cyanide distribution curves are very similar, each showing a large number of occurrences between 0.000 to 0.050 mg/ℓ and a long "tail" or skewed distribution beyond 0.25 mg/ℓ. Thus, where standards based on daily maximum levels are utilized, any cyanide treatment methods must be capable of handling wide fluctuations in inlet cyanide concentrations. Figures 4 and 5, indicate that any cyanide treatment system must also be designed to handle extended periods of high cyanide loadings.

Typical refinery cyanide effluent levels are presented in Table 1. The range of cyanide levels for the eight refineries included in Table 1 goes from 0.005 mg/ℓ to 0.176 mg/ℓ for the mean cyanide discharged. The maximum levels discharged vary from 0.03 mg/ℓ to 0.730 mg/ℓ total cyanide. While cyanide is present in all eight refineries in Table 1, the magnitude of the effluent cyanide concentrations varies by a factor of 30 from the lowest to the highest discharger.

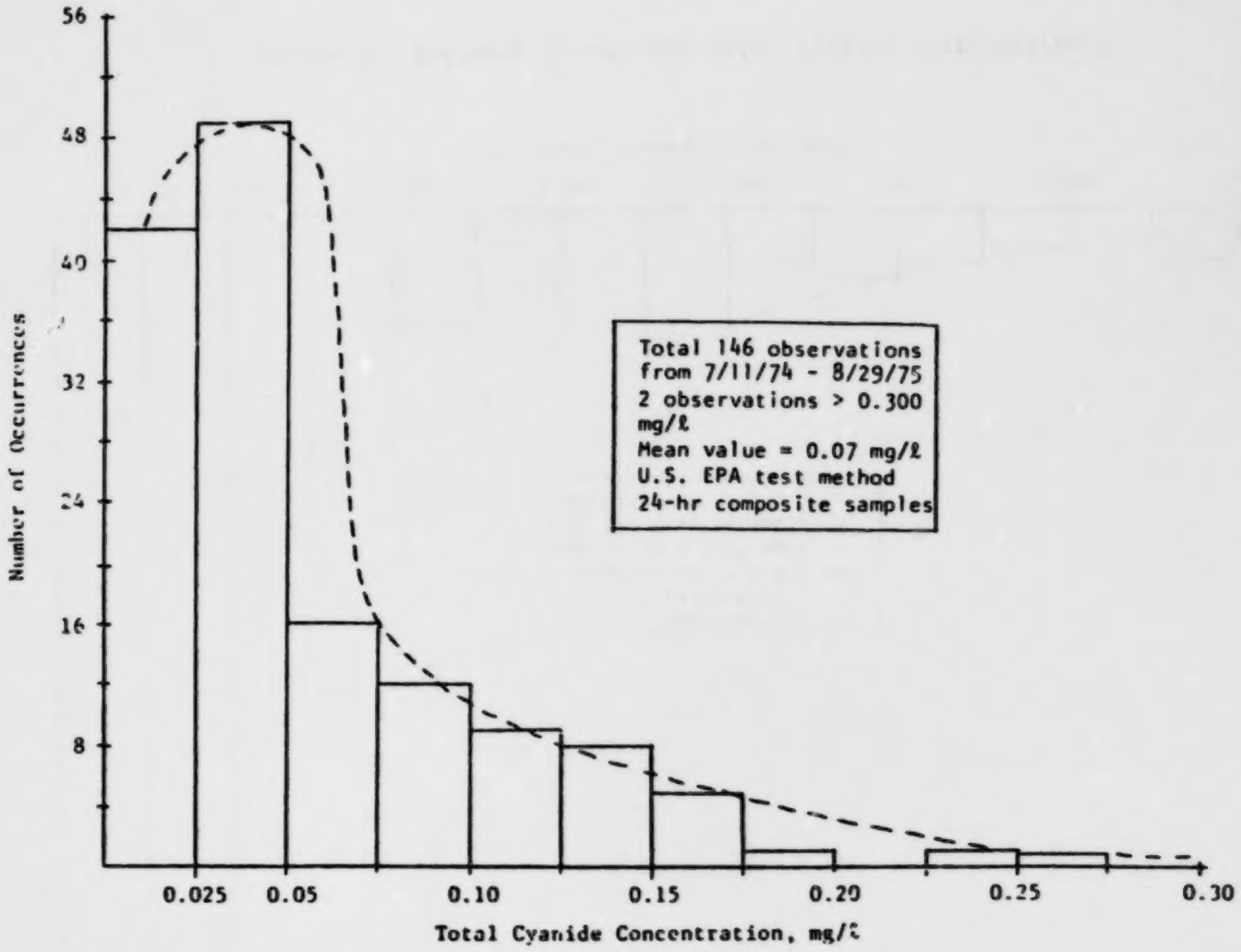


Figure 2. Refinery A--Effluent total cyanide distribution.[2]

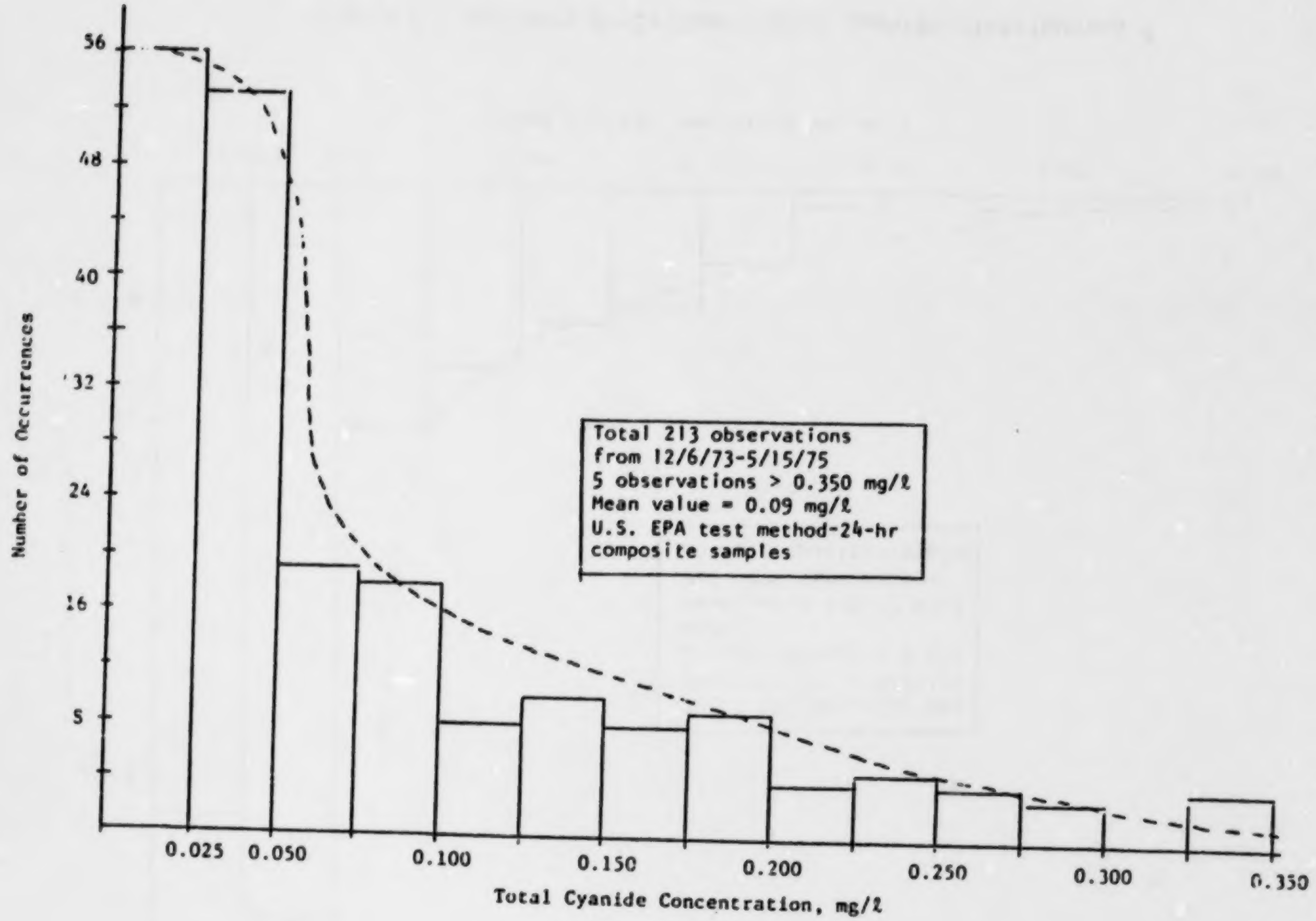


Figure 3. Refinery B--Effluent total cyanide distribution.[2]

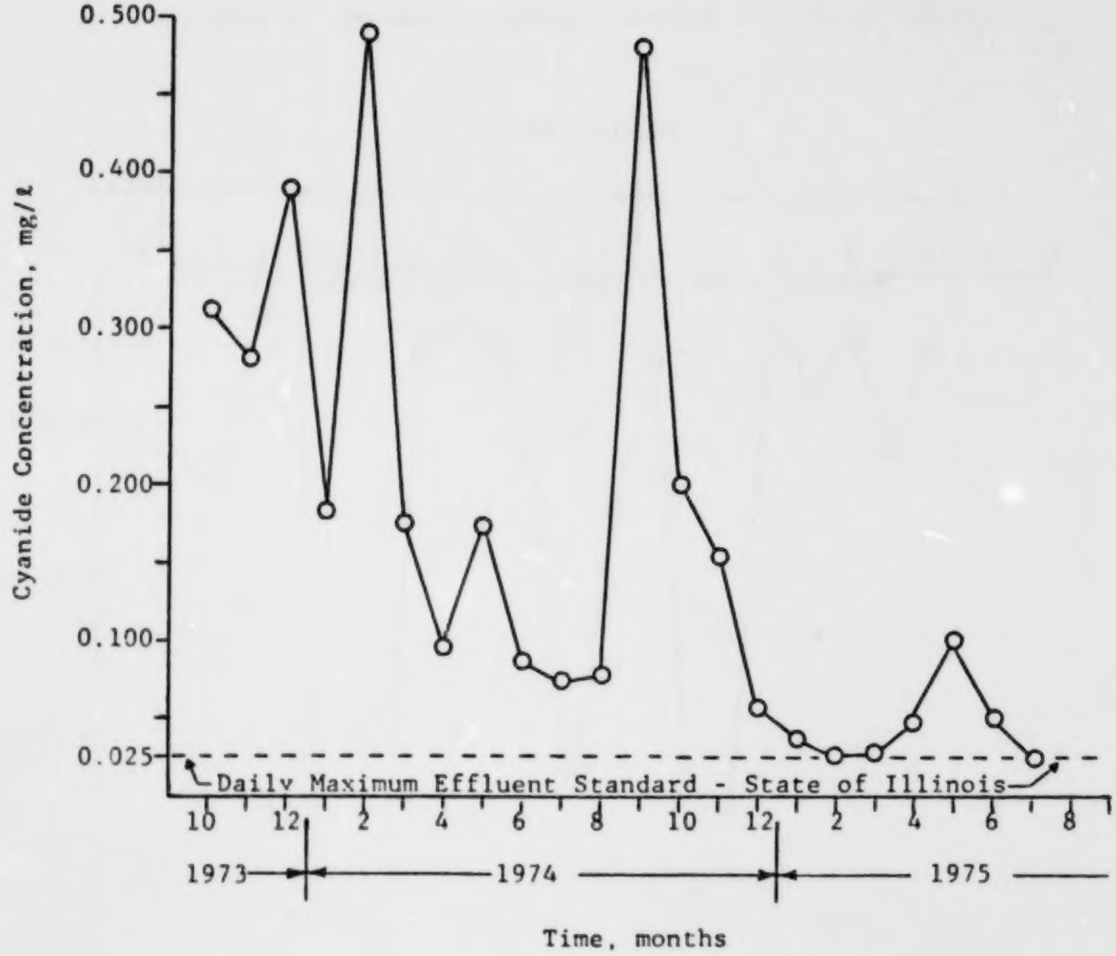


Figure 4. Refinery A--Monthly average cyanide discharged.[2]

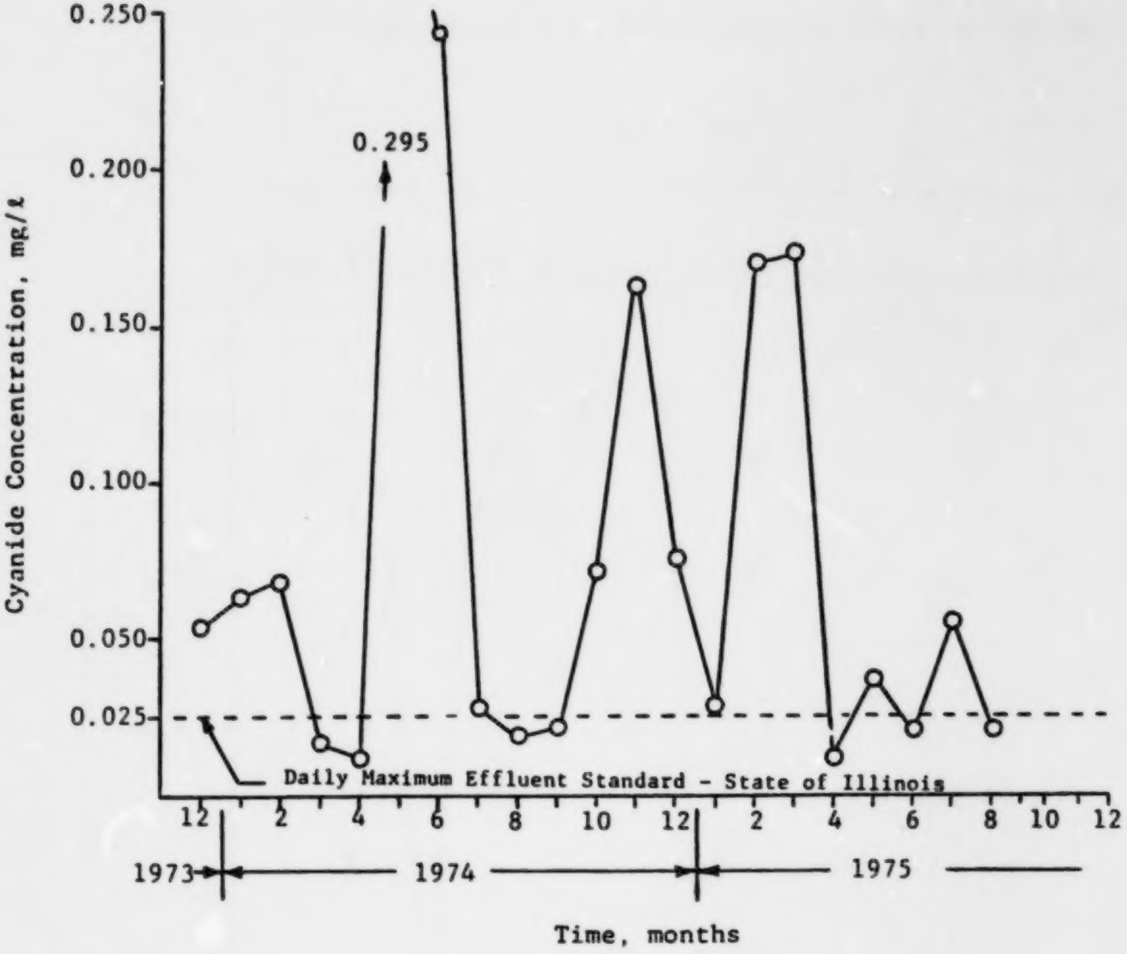


Figure 5. Refinery B--Monthly average cyanide discharged.[2]

TABLE 1. SUMMARY OF REFINERY CYANIDE LEVELS[2]

Refinery	Crude Rate (BPSD)	Effluent Flow Rate (MGD)	Average Total CN^- Discharged (mg/ℓ)	Maximum Total CN^- Daily Discharge (mg/ℓ)	Average Total CN^- Discharged		Average % Simple CN^- in Discharge (*)
					pounds/day	pounds/100,000 BPD Crude	
A	173,000	2.6	0.176	0.650	3.8	2.2	61
B	154,000	4.2	0.079	0.730	2.8	1.8	55
C	78,000	6.5	0.008	0.03	0.4	0.5	--
D	92,000	4.7	0.022	0.210	0.9	1.0	--
E	102,00	2.0	0.38	0.138	0.6	0.6	--
F	245,000	6.8	0.045	0.213	2.6	1.1	71
G	87,000	11.4	0.005	0.035	0.5	0.6	--
H	37,000	1.2	0.009	0.038	0.1	0.3	--

(*) As measured by the "Wood River Modification" of the "Roberts-Jackson method".

STATE AND FEDERAL REGULATIONS REGARDING CYANIDE

In a review of the existing state water quality and effluent standards, several of the standards stipulated are below analytical detectability. Table 2, which summarizes the variety of current regulations, also indicates that many states rely on a general, all-inclusive sentence to protect waters from toxic materials. Water quality standards relating to the bioassay tests on fish (Louisiana, Texas, New Jersey, Mississippi) are designed specifically to protect aquatic life.

In states where a range of values are used for different water quality designations, drinking water is governed by the higher values of 0.1 to 0.2 mg/ℓ cyanide. The lower levels of 0.005 to 0.01 typically represents limitations on streams which are aquatic life habitats. Only one state, New York, recognized a different toxicity for iron cyanides. The number of states specifying numerical values for their water quality standards is very small compared to the number of existing regulations. Even fewer states have adopted specific **effluent** limitations for dischargers. Only Delaware, Illinois, and Missouri have specified a numerical limitation on cyanide (0.05, 0.025, and 0.05 mg/ℓ respectively) for dischargers to their state waters.*

Thus, the states have established low values for water quality and effluent standards for cyanide in a variety of ways. While only three states have specific effluent standards for cyanide, rigorous enforcement of the water quality standards would require refineries in many states to reduce their cyanide levels prior to discharging.

At the federal level, both effluent and water quality standards will be adopted as part of the priority pollutant program. A water quality standard of 0.005 mg/ℓ of cyanide was recommended in the "Redbook."[3] Effluent standards, based on best available technology economically achieveable is required by July 1, 1984.[4]

EXISTING CYANIDE TREATMENT METHODS

Most exiting cyanide treatment methods are very effective in removing the simple cyanides. However, as shown previously in Table 1, refinery wastes contain both the simple and the complex cyanides. While the complex cyanide accounts for an average of approximately 50% of the total cyanide discharged by refineries, the percent complex cyanide is highly variable, ranging from 0% to 100%. Thus, any proposed treatment scheme must be capable or removing more than just the simple cyanides from refinery wastewaters.

Common treatment methods for cyanides include the following:

Chemical oxidation
Precipitation
Ion exchange
Biological decomposition
Adsorption and catalytic oxidation

---

*In 1978, the State of Illinois adopted a revised cyanide effluent limitation of 0.1 mg/ℓ monthly average and 0.2 mg/ℓ daily maximum.

TABLE 2. SUMMARY OF STATE STANDARDS FOR CYANIDE[5]

Water quality standard	State
1. General standard of free from toxic and harmful materials	Alabama, Arkansas, California, Colorado, Connecticut, Delaware, Georgia, Hawaii, Idaho, Kansas, Maine, Maryland, Massachusetts, Michigan, Missouri, Montana, Nebraska, New Mexico, North Carolina, Rhode Island, South Carolina, Tennessee, Utah, Vermont, Washington, Wisconsin, Wyoming
2. Not present greater than 1/10 96 hr TLm	Louisiana, Texas
3. Not present greater than 1/20 96 hr TLm	New Jersey
4. Not present greater than 1/10 48 hr TLM	Mississippi
5. 0.025 mg/ℓ	Illinois, Indiana, Iowa, Kentucky, Pennyslvania, West Virginia
6. None detectable	Florida
7. 0.01 - 0.02 mg/ℓ	Minnesota
8. As CN < 0.01 mg/ℓ As $Fe(CN)_6 \leq 0.4$ mg/ℓ	New York
9. 0.01 - 0.10 mg/ℓ	North Dakota
10. 0.005 (free) to 0.2 mg/ℓ (total)	Ohio
11. 0.005 - 0.01 mg/ℓ	Oregon
12. 0.2 mg/ℓ	Virginia
Effluent Standard	**State**
1. 0.05 mg/ℓ	Delaware, Missouri
2. 0.025 mg/ℓ	Illinois
3. No other state has specific effluent limit on cyanide	

Chemical oxidation, most notably alkaline chlorination, is very common in the electroplating industries and is very effective on the simple cyanides. For the complex cyanides, elevated temperatures, longer holding times, and more oxidant are required.[1,6] The presence of organics in refinery wastewaters limits the preacticability of chemical oxidation in the petroleum industry. The competitive oxidation rates of the organics result in excessive chemical consumption in order to destroy the cyanide to acceptable levels.[6]

Another alternative treatment method is precipitation which is limited to high cyanide-bearing streams. This limitation is due to the solubility of the metal cyanides formed during the precipitation reactions which is approximately 4 mg/ℓ as CN^-.[7] Ion exchange for the removal of cyanide has limited application in the refining industry because of the organics present in the wastewaters. Fouling and rapid deterioration of the resin preclude the use of ion exchange unless extensive pretreatment of the organics is utilized.

While the biological wastewater treatment systems present in most refineries remove some cyanide, the mechanisms involved are not well understood. Cyanide removals by biological treatment of greater than 99% have been achieved in the laboratory utilizing acclimated seed; however, laboratory biological treatment studies were ineffective in removing iron cyanides.[8]

One other cyanide treatment method available is adsorption with or without catalytic oxidation. Since the method investigated in this study can be classified as an adsorption with catalytic oxidation process, the existing technology in this area will be covered in the following section. Of the methods discussed, chemical oxidation is the only method currently capable of achieving cyanide levels of 0.025 to 0.1 mg/ℓ total cyanide. Chemical oxidation of the organics present in the wastewater, however, results in very high chemical requirements. Both the production of ozone and chlorine require energy-intensive processes. Thus, the existing cyanide treatment methods available to refineries are both energy and capital intensive.

If cyanide concentrations lower than those currently achieved are to be attained, a more economical treatment needs to be developed. This study investigates a potential low-cost method based upon adsorption with catalytic oxidation. In the following two sections, the previous work in this area is summarized, followed by a discussion of the potential low-cost application of this technology to refinery wastes.

ADSORPTION WITH CATALYTIC OXIDATION

Activated carbon has been investigated over the past twelve years both as an adsorbent and as a catalyst for the detoxification of cyanide. Bucksteeg[4] reported that passing potassium cyanide-bearing wastes over coal or coke resulted in removals in excess of 98%. Other forms of cyanide were also successfully removed by passing the waste over coal and coke. The mechanisms involved, according to Bucksteeg, were adsorption followed by catalytic oxidation, with the coal or coke acting as the oxidation catalyst. However, Bucksteeg concluded that removal of nickel and iron-cyanide complexes were attributable to only adsorption and not to any oxidation.

Activated carbon utilized as a catalyst for cyanide oxidation was patented by Kuhn in 1971.[10] The process requires an alkaline pH with a mixture of air and the cyanide-bearing waste pumped in a pulsating manner through a bed of activated carbon. No mention is made in the patent of the type of cyanide effectively removed, but it is probable that only simple cyanides would be affected.

In the early seventies, the Calgon Corporation developed a cyanide detoxification method utilizing catalytic oxidation on granular activated carbon.[11] Calgon's method is similar to Kuhn's process described previously, except that cupric ions are added to the wastewater along with oxygen prior to passing the cyanide-bearing waste through the granular activated carbon columns. According to Calgon, "cupric ions are added to the water to accelerate and increase the efficiency of the catalytic oxidation of cyanide by granular activated carbon."[11] In addition to improving the catalytic oxidation of the cyanide, "the presence of cupric ions results in the formation of copper cyanides, which have a greater adsorption capacity than copper or cyanide alone."[11]

Calgon's results indicated that a pH between 6.5 and 8, a constant copper feed, and dissolved oxygen throughout the carbon bed were necessary for maximum efficiency. Adsorption isotherms by Calgon demonstrated that the capacity of the granular carbon was limited to 2 or 3 mg of cyanide adsorbed per gram of carbon when no copper was used. However, the addition of copper increased the adsorption capacity of 25 mg CN^-/gm carbon without any dissolved oxygen present. When oxygen was maintained in the system, the adsorption sites were continuously regenerated through the oxidation of the cyanide. Tests with a 100 mg/ℓ cyanide in the feed resulted in cyanide effluent levels of less than 0.05 mg/ℓ and low effluent copper levels as long as the adsorption capacity of the copper on the carbon was not exceeded.[11]

In another test by Calgon, ferrous iron and cyanide were added to water and pumped through a granular activated carbon column, with high dissolved oxygen levels. The results, shown in Figure 6, indicate that iron cyanides can be oxidized, but at a slower rate than the copper cyanides. Calgon found that iron cyanides were difficult to treat for the following reasons:

1. The iron cyanide complex formation competes with the copper cyanide.

2. The iron cyanide complex is not adsorbed as well as copper cyanide.

3. The iron cyanide complex is more stable and harder to oxidize than the copper cyanides.

4. Iron will probably be present at low levels in most waters.

Calgon reported the results of a two-week pilot study on a coke plant waste, which was believed to contain iron cyanide. Over the two-week period, the cyanide was treated from an average inlet of 28.5 mg/ℓ to an average

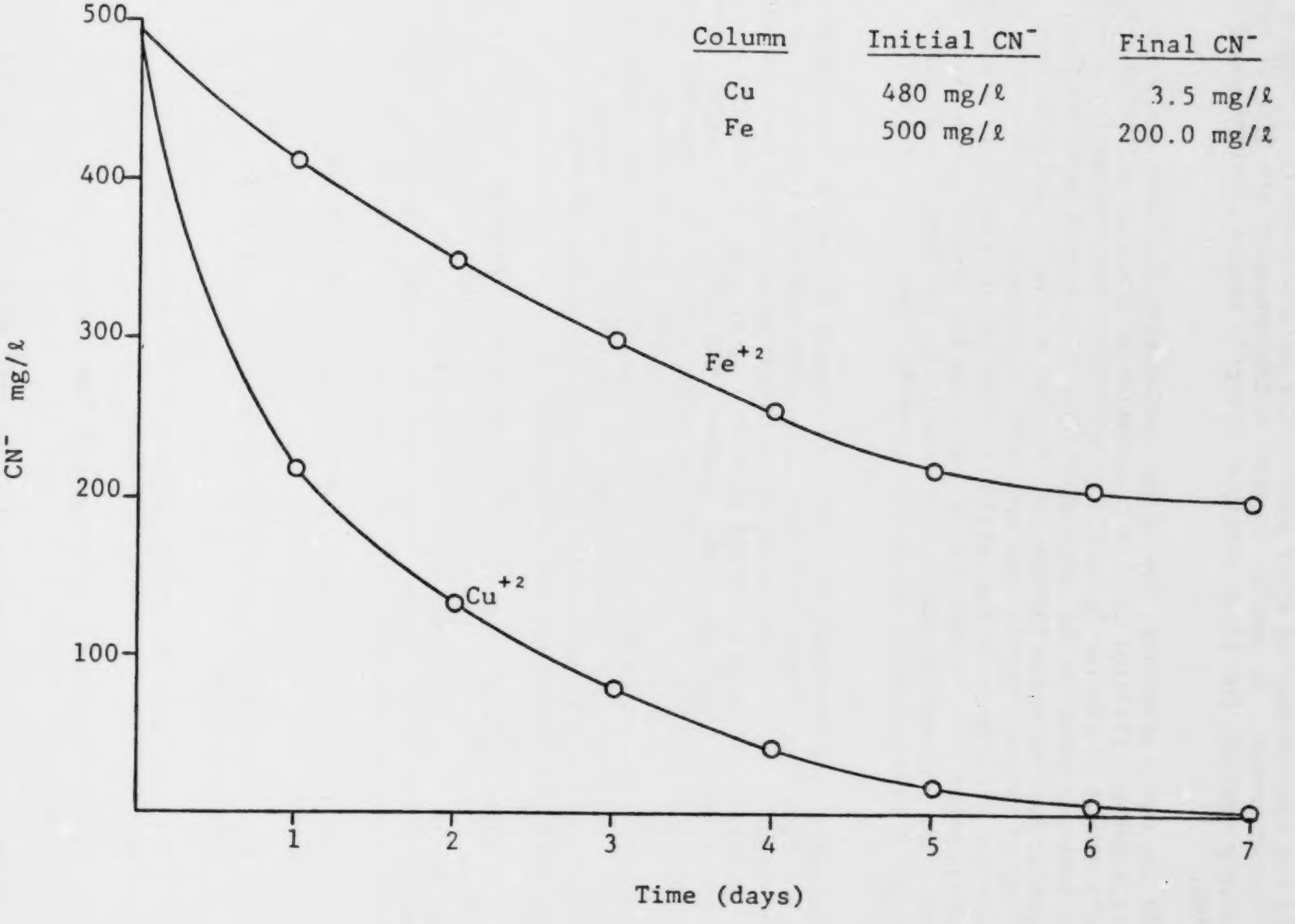


Figure 6. Iron cyanide disappearance rate.[11]

effluent of 0.41 mg/ℓ, or an average 98.5% removal. Considerable variation in the effluent cyanide concentration was observed, and this was attributed to the varying iron concentration of the wastewater.[11]

Based upon the work of Calgon, adsorption with catalytical oxidation is an effective method of reducing not only the simple cyanides, but potentially the complex or iron cyanides which are found in petroleum refinery wastewaters. Experience in this area is discussed in the following section along with the conceptual design for the process investigated in the present study.

POTENTIAL APPLICATION OF ADSORPTION WITH CATALYTIC OXIDATION TO REFINERY CYANIDE WASTEWATERS

The results reported by Calgon prompted one refinery to investigate adsorption with catalytic oxidation on their cyanide-bearing waste streams. The results of this study, as reported by the refinery, are presented below.[12]

"Based upon recommendations made by Calgon Corporation, two carbon adsorption pilot plants were evaluated. The first pilot plant was designed to investigate the merits of carbon adsorption on a smaller volume, high concentration cyanide bearing stream. It was conducted with the cooperation of Calgon's environmental engineering department. The second pilot plant, conducted without direct Calgon supervision, was designed to investigate the merits of carbon adsorption on an activated sludge clarifier effluent.

Calgon's analytic study of the first pilot plant led it to conclude that catalytic oxidation of adsorbed cyanide in the desalter stripper bottoms using granular activated carbon could not be achieved due to the presence of the stable ferrocyanide complex ($Fe(CN)_6^{-4}$). The report indicated that the ferrocyanide complex can be removed from the desalter stripper bottoms only if either a very equalized wastewater flow is obtained over an extended period of time, or a batch type treatment operation is installed to maintain proper pH control, the iron cyanide removal being very pH dependent. The report also emphasized that the efficiency of the catalytic oxidation cannot be determined unless the ferrocyanide complex has been removed.

The analysis of the data from the second pilot plant program indicated that carbon, under limited conditions, will adsorb cyanide from the final clarifier effluent. Carbon exhaustion, however, was calculated to be approximately 11.8 lb. carbon per 1000 per gallons of water treated. Based upon a flow rate of 3000 GPM and a total cyanide effluent concentration of 0.175 mg/ℓ, 51,000 pounds of carbon per day would be required to remove 6.3 pounds of cyanide per day. Further, attempts to catalytically oxidize the adsorbed cyanide, and thus regnerate the carbon, by the presence of excess oxygen and copper failed. Aeration actually caused an increase in carbon column cyanide effluent concentration. It was determined, therefore, that a carbon-adsorption system could not produce sufficient cyanide removal **on any practical scale** under conditions prevalent at the Union Oil, Lemont refinery."

The above results indicate that equalization and pH control are important to the success of the system. This finding is similar to Calgon's results on the other industrial wastes investigated.[11] The increase in cyanide observed upon aeration suggests that the iron cyanides were being adsorbed at a faster rate than they were being oxidized. Thus an accumulation of cyanides in the column resulted, which, with a change in conditions, were released into the effluent. Assuming that equalization, pH control, and a bed of granular activated carbon adequately sized to allow sufficient time for cyanide oxidation could be provided, the major problem then becomes one of cost. The calculated consumption rate of 51,000 pounds per day of granular carbon places the economics of this system in the same category, very expensive, as the the high temperature chlorination and ozonation processes.

Utilizing the findings obtained to date with adsorption and catalytic oxidation, a potential low-cost process for removing cyanides from petroleum refineries was conceived. The process and its operational advantages are described in this section prior to presenting the performance results in the next chapter.

The major drawbacks with the Calgon process for refinery waste streams are the large initial capital expenditure and the high rate of carbon exhaustion because of the organic loading. The conceptualized process evaluated in this study involves the addition of PAC and $CuCl_2$ directly into the activated sludge unit. The advantages of this process are a minimal capital expenditure and potentially a lower carbon exhaustion rate because of biological regeneration of the carbon. There are numerous other advantages from the addition of PAC to an activated sludge unit. If the cost of the carbon is allocated among all of the benefits, the cost of this cyanide removal process is even less. An excellent case history of PAC benefits was provided by Flynn and Barry.[13] A summary of the potential benefits of PAC addition to an activated sludge plant was provided by Adams;[14] and these benefits are listed below:

1. It will improve BOD and COD removals despite hydraulic and organic overloads.

2. It will aid solids settling, decrease effluent solids, and increased sludge solids.

3. It will adsorb dyes and toxic components that are either not treated biologically or are poisonous to the biological system.

4. It will prevent sludge bulking over broader food to micro-organism ranges.

5. It will effectively increase plant capacity at little or no additional capital investment.

6. It will provide more uniform plant operation and effluent quality, especially during periods of widely varying organic or hydraulic loads.

The potential advantages of the $PAC/CuCl_2$ addition directly into the activated sludge unit over the previous cyanide destruction methods are numerous. As stated previously, the capital expenditure is minimal and the carbon exhaustion rate should be lower, thus consuming less carbon. In addition, PAC costs approximately half of the cost of granular activated carbon (GAC). PAC also has a greater surface area per unit weight of carbon. The contact times between the cyanide and carbon are longer in the aeration tank (6-12 hours) as opposed to GAC columns (15-60 minutes), although GAC columns have a much higher carbon:wastewater ratio. In addition, the PAC remains in the system for the time equal to the sludge age (10-25 days) which should provide a sufficiently long period for oxidation of the adsorbed cyanides. From the refinery investigation with the GAC column, the rate of oxidation of the cyanides may be the limiting loading factor.

Based upon the conceived process for cyanide removal, this research program was undertaken to ascertain the potentail feasibility of the process. There were numerous questions that had to be addressed before the overall viability of the process could be determined. These questions were:

1. What effect will the copper have on the overall performance of the activated sludge system?

2. Can the cyanides be reduced to effluent levels of 0.025 to 0.1 mg/ℓ total cyanide?

3. Will the biological solids (mixed liquor suspended solids, MLSS) and/or organics present interfere with cyanide adsorption and/or cyanide oxidation?

4. Will the iron cyanides oxidize once adsorbed onto the carbon, or will these compounds accumulate in the system?

5. Does the removal efficiency increase with higher initial cyanide concentrations?

6. What fraction of the copper added to the system will be present in the treated effluent?

7. What influence on the overall performance does each of the following variables have:

    - carbon dose
    - cupric chloride dose
    - dissolved oxygen level
    - mode of cupric chloride addition
    - pH
    - hydraulic residence time
    - sludge age

If the cyanide can not be treated to levels of 0.025 to 0.1 mg/ℓ, and the removal efficiency improves with increasing inlet cyanide concentrations, then in-plant treatment may be more effective. The cyanide-bearing stripped sour water is the in-plant stream with the greatest potential. It could be treated before or after the desalter, prior to discharging to the sewer.

A small activated sludge unit could be constructed, designed and operated to maximize the removal of cyanide through the addition of PAC and $CuCl_2$. Directing the stripped sour water to the cooling tower and adding low concentrations (25-100 mg/ℓ) of carbon and $CuCl_2$ to the cooling water system may also be feasible and would require minimal capital expenditure.

Until the basic chemistry is understood, the most advantageous treatment scheme can not be determined. The experimental program described in the following sections was designed to provide the information needed to evaluate the process for cyanide removal. The first phase of the program was directed toward obtaining a basic understanding of the process. The second phase then applied this understanding and the most promising treatment scheme to determine the overall viability of the process.

SECTION 4

EXPERIMENTAL SYSTEMS AND ANALYTICAL METHODS

EXPERIMENTAL SET UP

The experimental development of design criteria for the use of activated carbon and cupric ions for the removal of cyanide in an activated sludge waste treatment system proceeded in two phases. Phase I consisted of 13 batch tests for the determination of optimal levels of the various operational parameters. This part of the study was conducted in batch reactors with tap water spiked with known concentrations of cyanide and no biological activity. Phase II tests were conducted with actual refinery wastewater in a continuous flow, activated sludge waste treatment system. The Phase I batch tests were designed to determine the effect of various parameters on cyanide removal. These parameters included:

pH
Mode of $CuCl_2$ addition
$CuCl_2$ dosage
Type of carbon
Carbon concentration
Initial cyanide concentration

The reactors used for the batch tests were fabricated from plexi-glass and had a total capacity of 12 liters, as shown in Figure 7. For Phase I the baffle was removed and the overflow ports covered over. This provided for a complete mixed batch reactor, the agitation being provided by the air introduced through a diffuser stone located near the bottom of the reactor. The agitation took the form of a gentle rolling of the reactor contents.

The synthetic waste utilized in the batch tests consisted of stock solutions of potassium ferricyanide and ferrocyanide, (1000 mg/ℓ as CN^-), in distilled water. These solutions were prepared on a monthly basis. The PAC was treated prior to these tests by first washing in distilled water. drying in a vacuum oven, then storing in a desiccator until weighing.

The cupric ions were made up in a stock solution of $CuCl_2$ (1000 mg/ℓ as Cu) in distilled water, with 2 ml of sulfuric acid (H_2SO_4) added per liter of stock solution. Preparation of the reactors for the batch tests consisted of the following procedure.

1. Charge the reactors with 11 ℓ of tap water (pH∿8.3) and aerate for a minimum of one-half hour.

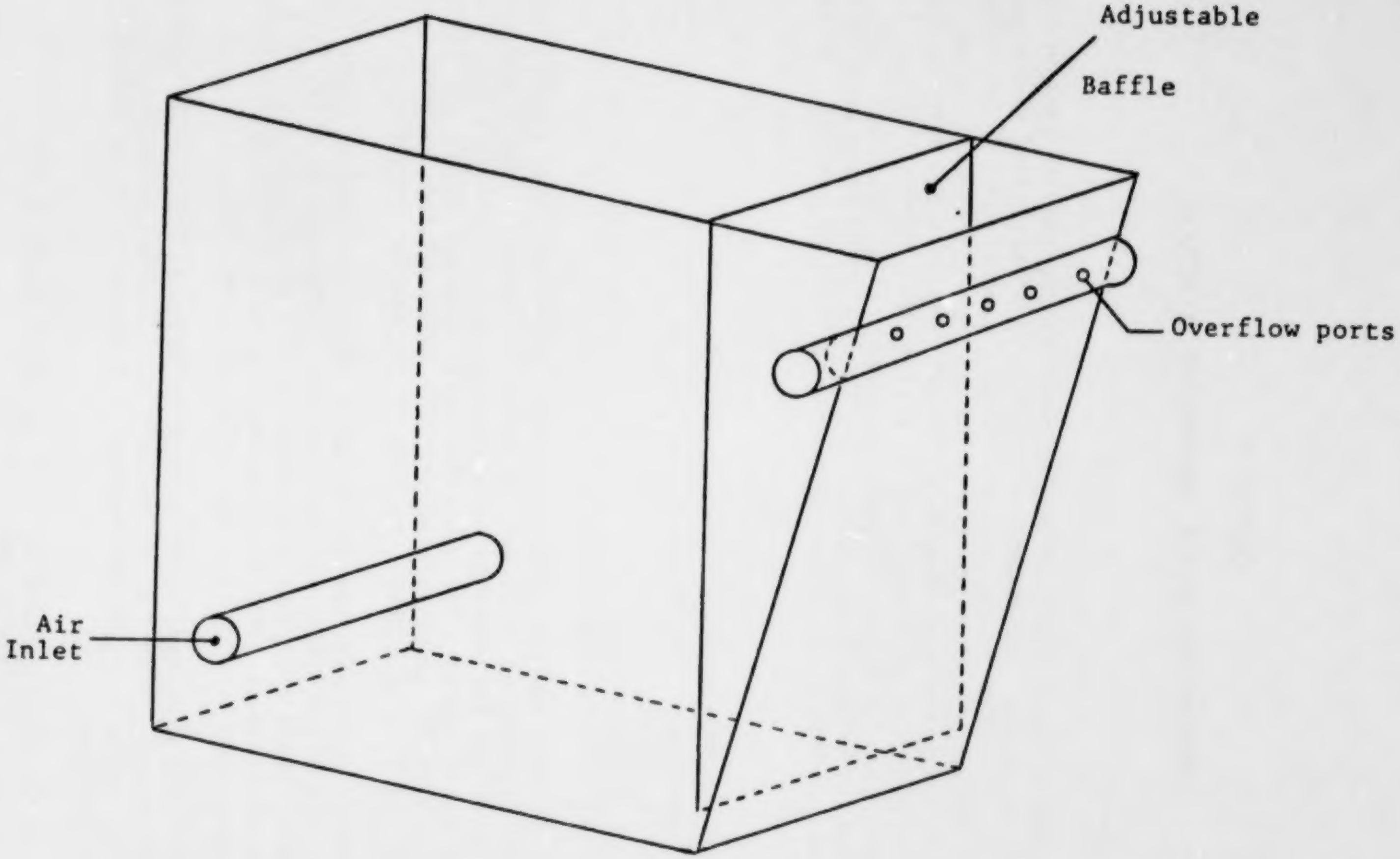

Adjustable
Baffle
Overflow ports
Air
Inlet

Figure 7. Experimental reactor.

2. Adjust the pH as necessary. ($NaOH$ or H_2SO_4)

3. Pipette the required amount of cyanide from the stock solution. (1000 mg/ℓ as CN^-)

4. Add the $CuCl_2$ from the stock solution (1000 mg/ℓ as Cu) and the desired amount of carbon.

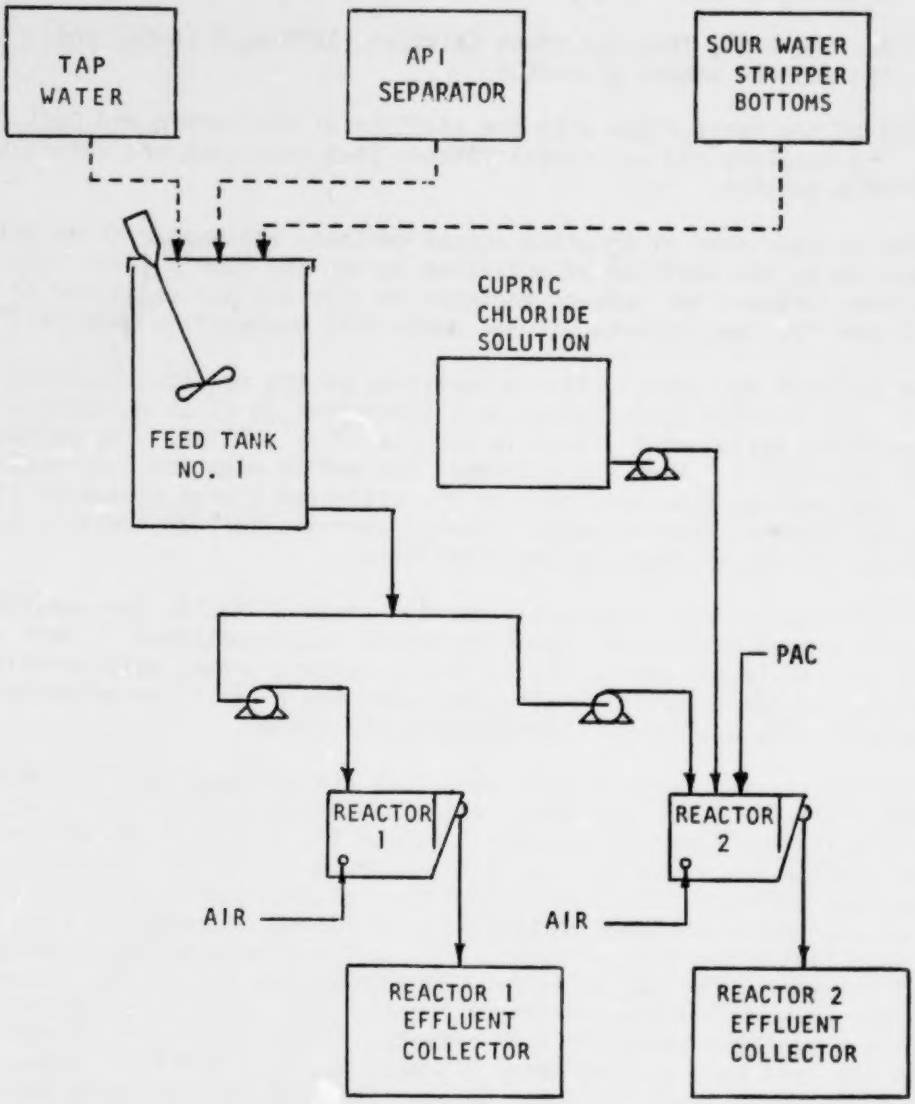
The timing of the tests began with the addition of the carbon and $CuCl_2$ to the system. The sampling and analytical methods that were used are described later in this section.

Phase II consisted of treating actual refinery wastewater in an activated sludge system by the addition of activated carbon and cupric ions. The single stage system followed the pattern depicted in Figure 8 and consisted of a common feed tank for two activated sludge units that operated in parallel.

The physical equipment utilized consisted of the reactors depicted in Figure 7. The reactor compartments were fabricated so as to maintain 8 liters in the aeration basin and 2 liters in the clarifier section. The baffle was adjusted for a 1.5 - 2.5 cm space between the baffle edge and the reactor bottom. The average flow rate through the activated sludge system of 19 liters per day resulted in a detention time of approximately 10 hours in the aeration basin and 2.5 hours in the clarifier.

To initiate biological activity for the Phase II tests, the aeration basins were seeded with mixed liquor suspended solids obtained in part from a refinery aerated lagoon and partially from a culture grown, with phenols as a food supply, in the laboratory. The feed tank was a 115 liter polyethylene tank equipped with a mixer for homogenizing the system.

The initial feed solution considered was the effluent from the American Petroleum Institute (API) separator, which contained cyanide levels of less than 0.05 mg/ℓ. In order to accurately assess the potential of the process, a higher cyanide level was desired than was found in the API separator effluent from this refinery. Initially, 42 liters of API separator effluent, 21 liters of sour water stripper bottoms, and 21 liters of tap water were charged to the feed tank three days per week. The stripper bottoms had a cyanide level of 1-2 mg/ℓ. The tap water was added to reduce the BOD and phenol concentrations to more "typical" refinery levels. To prevent the nutrient level from being a limiting factor in the activated sludge units, the phosphorous level in the feed tank was increased 2-3 mg/ℓ (as P). The feed composition was modified approximately half-way through Phase II because the cyanide removal across the control reactor was over 90% and the effluent cyanides were thus less than 0.05 mg/ℓ. To increase the effluent cyanide levels the make-up to the feed tank was changed to 21 liters of API separator effluent, 42 liters of sour water stripper bottoms, and 21 liters of tap water. This effectively increased the inlet total cyanide level to 0.50 - 0.80 mg/ℓ and a corresponding increase in the effluent cyanide concentration.



TAP WATER
API SEPARATOR
SOUR WATER STRIPPER BOTTOMS
CUPRIC CHLORIDE SOLUTION
FEED TANK NO. 1
PAC
REACTOR 1
REACTOR 2
AIR
AIR
REACTOR 1 EFFLUENT COLLECTOR
REACTOR 2 EFFLUENT COLLECTOR

Figure 8. Single stage activated sludge system.

The wastewater was pumped from the feed tank to reactors 1 and 2 (control and test reactors, respectively), via a variable speed "Master-Flex" tubing pump with dual pump heads. The pump was controlled by a 30-minute cycle timer set for pumping 70% of the time. The 9 minute "rest" each half-hour allowed the pump and tubing to cool, which provided for longer tubing and pump life.

The sludge age was maintained in each reactor by wasting sludge one a day. To waste sludge, the baffle between the aeration and clarifier section was removed, the side walls scraped to remove any growth, and a beaker was dipped into the reactor to remove the sludge. The sludge was poured into a graduated cylinder for settling, and the baffle was then immediately replaced between the clarifier and aeration section. After the solids settled in the graduated cylinder for one-half hour, the clear supernatant was returned to the aeration basin.

The effluent from each reactor was collected in 19 liter glass bottles that were held in ice buckets to maintain the integrity of the samples. After the sludge was wasted each morning, the liquid level in the clarifier was below the overflow weir for 30 to 45 minutes. The composite samples were not started each day until approximately 2 hours after the sludge was wasted, to allow the system to equilibrate. Then, each morning, just prior to wasting sludge the composite samples were taken for the purpose of daily analysis. Thus, the composite samples were only 22 hour samples, with 2 hours allowed each day for the system to settle down after the sludge was wasted.

Cupric chloride addition to the test reactor was accomplished by making up a 300 mℓ solution with the desired quantity of copper in it. This solution was then pumped into the test reactor by means of a small tubing cassette pump. This pump was also controlled by the 30 minute cycle timer. The flow rate was adjusted so that the $CuCl_2$ solution was completely added during each 24 hour period.

The last test in Phase II consisted of a two-stage activated sludge system with cyanide removal in the second stage. The feed for the second stage test was composed of the effluent from control reactor 1 mixed with 5 liters per day of stripper bottoms and 15 liters per day of tap water to provide sufficient wastewater for two second-stage units. Both the second-stage test and control reactors were operated with a common 50 liter polyethylene feed tank. The operation of the second-stage test was identical to the previous tests described earlier, including flow rates, copper and carbon addition, and sample collection.

SAMPLING PROCEDURE

This section described the procedures followed for obtaining samples. In Phase I, or the batch tests, cyanide was the key parameter which was monitored. Grab samples were taken at various time intervals and filtered. Cyanide analyses were then performed both on the filtrate and on the filter cake. The filter cake was resuspended in distilled water immediately after filtering and then preserved until the cyanide content was analyzed. Although three different procedures were utilized in attempting to determine the quantity of cyanide per unit weight of solids, none of the three proved satisfactory. The first technique consisted of refiltering the carbon fines from the cyanide distilling flask after the cyanide analysis was complete. Control tests indicated a loss of solids of 15-25% occurred as a result of this procedure. Duplicate solids samples were also collected, one for cyanide analysis and one for solids analysis. The variation in the solids level from duplicate samples was approximately 25%. This third procedure attempted was to dry and weigh the solids prior to cyanide analysis, but this also gave very inconsistent results. Additional information on the measurement of the cyanide on the carbon is included in the following section.

Phase II tests included the operation of biological waste treatment systems. The actual performances of the activated sludge units were measured by the removal efficiences of various pollutants. All inlet samples were taken from the feed tank as grab samples, while the effluent samples were all collected from the 22-hour composite samples. The inlet and effluents were monitored for the following pollutants:

Parameter	Sample Frequency, No. of days/week	Comments
Cyanide (CN^-)	7	----------
Phenols	3	Stopped testing for phenols midway through Phase II
Biochemical Oxygen Demand (BOD_5)	5	----------
Total Organic Carbon (TOC)	3	Filtered samples only during the last test
Chemical Oxygen Demand (COD)	3	Taken only during last part of Phase II on filtered samples
Suspended Solids (SS)	3	----------

As indicated above, only the COD and TOC samples during the last test were filtered, all other analyses were performed on unfiltered samples.

The performance of each activated sludge unit was also monitored by sampling for the following biological parameters.

Parameter	Sampling Frequency, No. of days/week
Mixed Liquor Suspended Solids (MLSS)	3
Settleability	7
Through-put of treated wastewater	7

ANALYTICAL METHODS

The analytical methods used during this program were in accordance with those outlined in "Methods for Chemical Analysis of Water and Wastes."[15] The cyanide test procedure was modified slightly to improve the precision at the lower cyanide concentrations. These modifications to the cyanide procedure are described below.

Cuprous Chloride Reagent

The EPA procedure was modified to the following:

1. Weigh 10 g of Cu_2Cl_2 and place in a 500 ml reagent bottle.

2. Wash by decantation four times with 250 ml portions of dilute sulfuric acid (H_2SO_4, 1 + 49).

3. Wash by decantation two times with 250 ml portions of distilled water.

4. Dilute Cu_2Cl_2 solution to 250 ml with distilled water.

5. Add 50 ml HCl (sp. gravity 1.19) and continue adding 1 ml portions of the acid until solution is clear and all cyrstals have dissolved.

6. Add 100 ml of distilled water and enough HCl to dissolve any crystals that form. Dilute to 500 ml with distilled water. Solution should be light green.

7. Store in a tightly stoppered bottle containing a few lengths of pure copper wire.

Procedure for Cyanide Analysis

The EPA procedure is presented below, with the modifications utilized in this study underlined.

8.1 Place 500 ml of sample, or an aliquote diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1) to the adsorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube. Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 50 ml 1:1 sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 10 ml of Cu_2Cl_2 reagent (7.4) into the air inlet and wash down with a stream of water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for two hours. Turn off heat and continue the air flow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.5 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.6 Withdraw 20 ml of the solution from the volumetric flask and transfer to a 50 ml volumetric flask. Add 15 ml of sodium phosphate solution (7.6) and 2.0 ml of Chloramine T solution (7.12) and mix. Immediately add 5.0 ml pyridine-barbituric acid solution (7.13.1), mix and bring to mark with distilled water and mix again.

8.7 When using pyridine-barbituric acid, allow 6 minutes for color development than read absorbance at 578 nm in a 1.0 cm cell immediately.

8.8 - 8.11 No change in USEPA procedure.

The above modifications to the EPA procedure have been utilized by some of the refineries in Illinois, and the refineries have found that the above modifications yield more precise results on refinery wastewaters. Two types of distilling glassware set-ups are recommended by the EPA test method. The one utilized in this project is shown in Figure 9.

Other analytical equipment utilized was a Beckman Model 915 for total organic carbon (TOC) measurements. Copper analyses were performed on a Perkin Elmer Model 360, Atomic Adsorption Spectrophotometer.

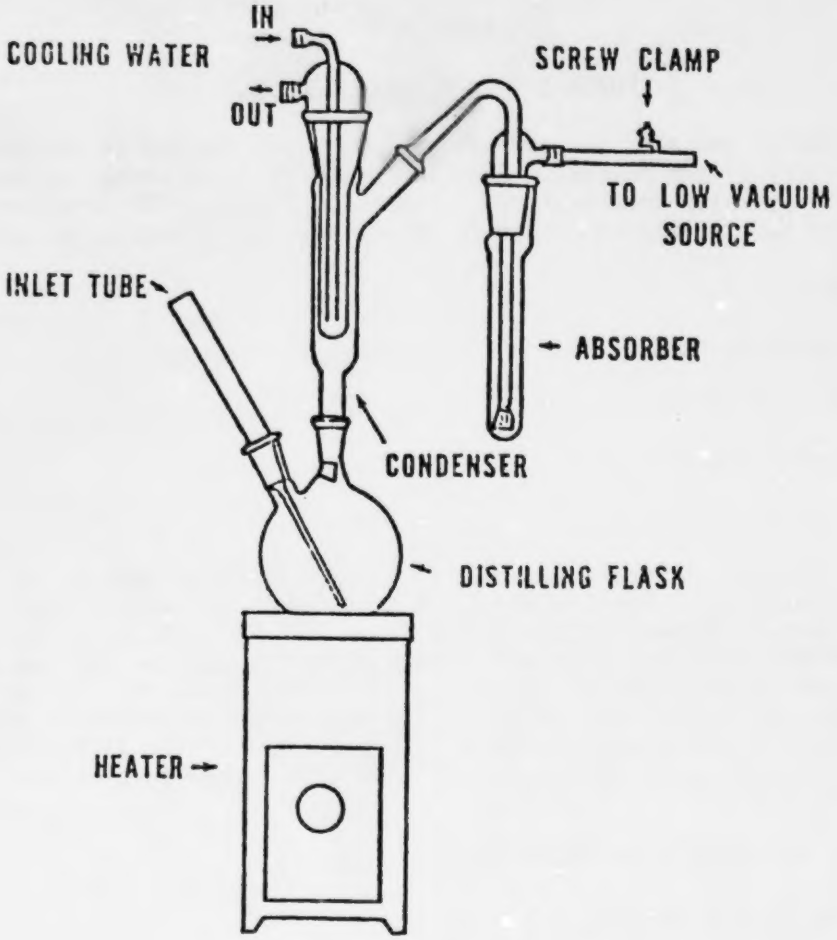

IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

Figure 9. Cyanide distillation apparatus.[15]

SECTION 5

PHASE I - EXPERIMENTAL RESULTS

The initial phase of the experimental work was limited to defining the basic chemistry of the process. A series of batch tests using tap water spiked with potassium ferrocyanide or potassium ferricyanide were performed to delineate the importance of the following five operating variables:

1. pH
2. copper dosage
3. mode of copper addition
4. carbon dosage
5. type of carbon

For each test, filtrate samples for cyanide analysis were collected at times of 15 minutes, 1 hour, 6 hours, 24 hours, and for certain tests 48 hours and/or 72 hours. Carbon samples were also periodically collected for determination of the quantity of cyanide remaining on the carbon. Of the 275 cyanide analyses performed during Phase I, (excluding standards), 79% of the samples were analyzed within 24 hours, 12% were analyzed within 48 hours, and the remaining 9% were analyzed within 72 hours. All of the filtrate samples were analyzed withing 48 hours, thus only certain carbon samples were held 72 hours before analysis.

DESCRIPTION AND RESULTS OF BATCH TESTS

pH Effect on Cyanide Removal

The first operating variable investigated in the batch tests was pH. Two types of cyanide, potassium ferrocyanide and potassium ferricyanide, were utilized each at three pH levels. The results of the ferrocyanide test runs, presented graphically in Figure 10, indicate that the rate of cyanide removal increased with decreasing pH. The equilibrium cyanide level, which was considered to occur after 24 hours, was lower at the lower pH level. The lower pH apparently changed the surface properties of the PAC resulting in a greater affinity for the iron cyanides.

The results of the ferricyanide tests were found to be very similar to the ferrocyanide tests, as expected. This second series was only carried out for 6 hours, with the results shown in Table 3.

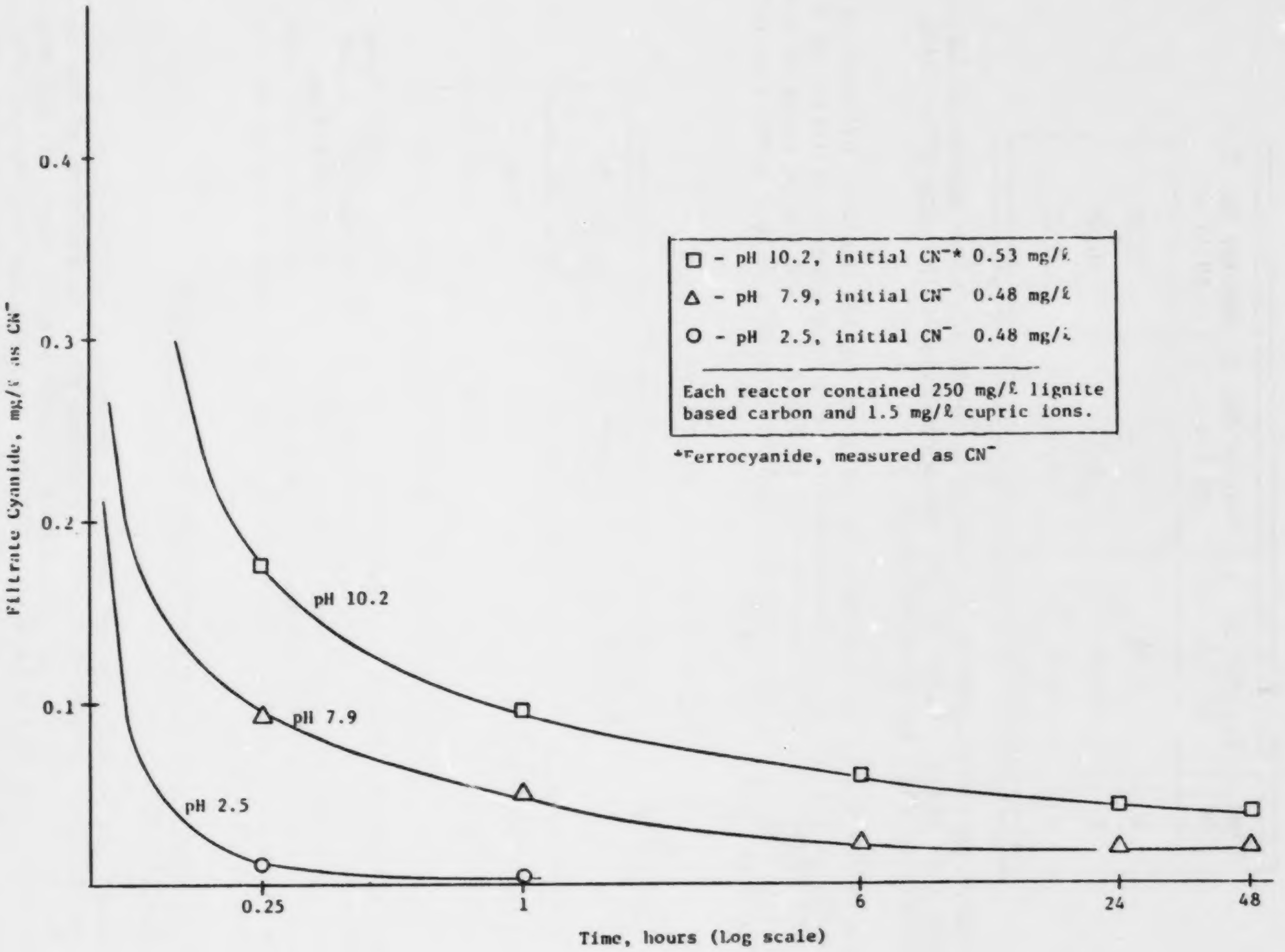


Figure 10. pH effect on rate of cyanide removal.

TABLE 3. RESULTS OF pH EFFECT ON FERRICYANIDE REMOVAL

Time, hr	Reactor No. 1 pH 3.0	Reactor No. 2 pH 7.0	Reactor No. 3 pH 11.0
0	0.44	0.50	0.52
1	<0.01	0.11	0.09
6	<0.01	0.01	0.05

Thus, ferricyanide removal is influenced by pH in a similar manner to ferrocyanide; that is, the lower the pH, the more rapid is the adsorption rate, and the higher the removal efficiency.

While the low pH is desirable for maximum cyanide removal, effluent copper levels at the low pH are unacceptable. Filtrate samples collected at 6 hours for copper analysis are presented in Table 4. The low pH range of 2.5 to 3.0 resulted in effluent copper concentrations of 1.7 to 1.8 mg/ℓ, as compared to 0.02 to 0.05 mg/ℓ at the higher pH values.

TABLE 4. FILTRATE COPPER LEVELS, mg/ℓ

	Reactor No. 1 pH 2.5 - 3.0	Reactor No. 2 pH 7.0 - 7.9	Reactor No. 3 pH 10.2 - 11.0
ferrocyanide	1.8	0.05	0.05
ferricyanide	1.7	0.05	0.02

While cyanide removal is enhanced in lower pH solutions, copper levels are not satisfactory. At near-neutral pH values, cyanide removals of 94% and 98% were obtained, while filtrate copper levels of 0.05 mg/ℓ were also achieved. Thus, for the remainder of Phase I, no pH adjustments were made, and the ambient pH ranging from 8.3 to 8.4 was considered adequate for the remaining batch tests.

Effect of Cupric Ion Concentration and Mode of Addition on Cyanide Removal

Copper can be added by two different techniques, either directly into the aeration basin or adsorbed onto the carbon prior to addition of the carbon. Two series of tests were conducted to determine if there was any significant difference in the mode of addition. Each reactor was charged with 250 mg/ℓ of lignite-type carbon, and ferrocyanide was used as the cyanide source. The results are presented in Tables 5 and 6.

TABLE 5. MODE OF COPPER ADDITION, 1.5 mg/ℓ INITIAL COPPER DOSE

Time, hr	Cyanide concentration, mg/ℓ		
	Copper adsorbed onto carbon	Copper added directly to basin	Copper added directly to basin
0	0.52	0.39	0.39
0.25	0.065	0.060	0.040
1.0	0.16	0.040	0.025
6.0	<0.01	<0.01	0.010
48	---	---	<0.01
72	<0.01	0.013	---

TABLE 6. MODE OF COPPER ADDITION, 0.5 mg/ℓ INITIAL COPPER DOSE

Time, hr	Cyanide concentration, mg/ℓ	
	Copper adsorbed onto carbon	Copper added directly to basin
0	0.48	0.37
0.25	0.20	0.17
1.0	0.16	0.13
6.0	0.17	0.14
48	0.12	0.12

Tables 5 and 6 indicate there is little, if any, difference in cyanide removal based upon the mode of addition. The filtrate copper levels were also unaffected by the mode of addition. No further studies were conducted regarding the mode of copper addition, and for the remainder of the tests, the copper was added directly into the aeration basin.

Numerous tests were conducted with varying copper concentrations, and the typical results are presented graphically in Figure 11. (All of the test results are tabulated in the Appendix). Such data indicated that the copper dose is an important factor in the cyanide removal process. For example, with 250 mg/ℓ of the lignite carbon and no copper, an equilibrium cyanide level of 0.28 mg/ℓ was achieved; however, with 1.0 mg/ℓ copper added to the same system, equilibrium cyanide levels as low as 0.010 mg/ℓ were achieved.

Effect of Carbon Type and Concentration on Cyanide Removal

Two types of PAC, lignin-based (Aqua Nuchar) and lignite-based (Hydrodarco C), were evaluated. The performance of each carbon type was evaluated throughout a range of carbon and copper concentrations. The cyanide levels achieved with each carbon are presented in Figure 12. The lignite-based carbon appeared to be superior for all levels tested; however, as the copper dosage increases, the effect of carbon type is diminshed.

Utilizing 1.0 mg/ℓ of the copper and ferricyanide as the new cyanide source, the lignin and lignite carbons were compared at a dosage level of 250 mg/ℓ carbon. The results from this test are presented in Table 7. The lignin carbon was found to be more effective on the ferricyanide, which is just the opposite of the results with the ferrocyanide.

Comparing Figure 11 to Figure 12, it is apparent that the equilibrium cyanide achieved is influenced more by the copper dosage than by the carbon dosage. For example, a doubling in the copper level has a much greater impact on the final cyanide concentration than does a doubling in the carbon level. These qualitative deductions are further confirmed in the regression analysis which follows.

The carbon dosage also influences the copper concentration found in the filtrate, as does the initial copper dosage. While the above results suggest that higher inital copper and lower carbon levels may be the most economical approach for removal of cyanide, the filtrate copper level is a limiting constraint, which is discussed in the following section.

Effluent Copper Levels

The "acceptable" effluent copper level is an important operating constraint and will vary for each refinery, depending upon water usage, state effluent standard, and water quality standards. An effluent copper level of 0.1 mg/ℓ was assumed to be an "acceptable" level to achieve during the batch tests, and this was used as a criterion for all filtrate samples.

The filtrate copper samples, all collected 6 hours after initiating each batch test, are summarized in Table 8. Data for both carbon types were

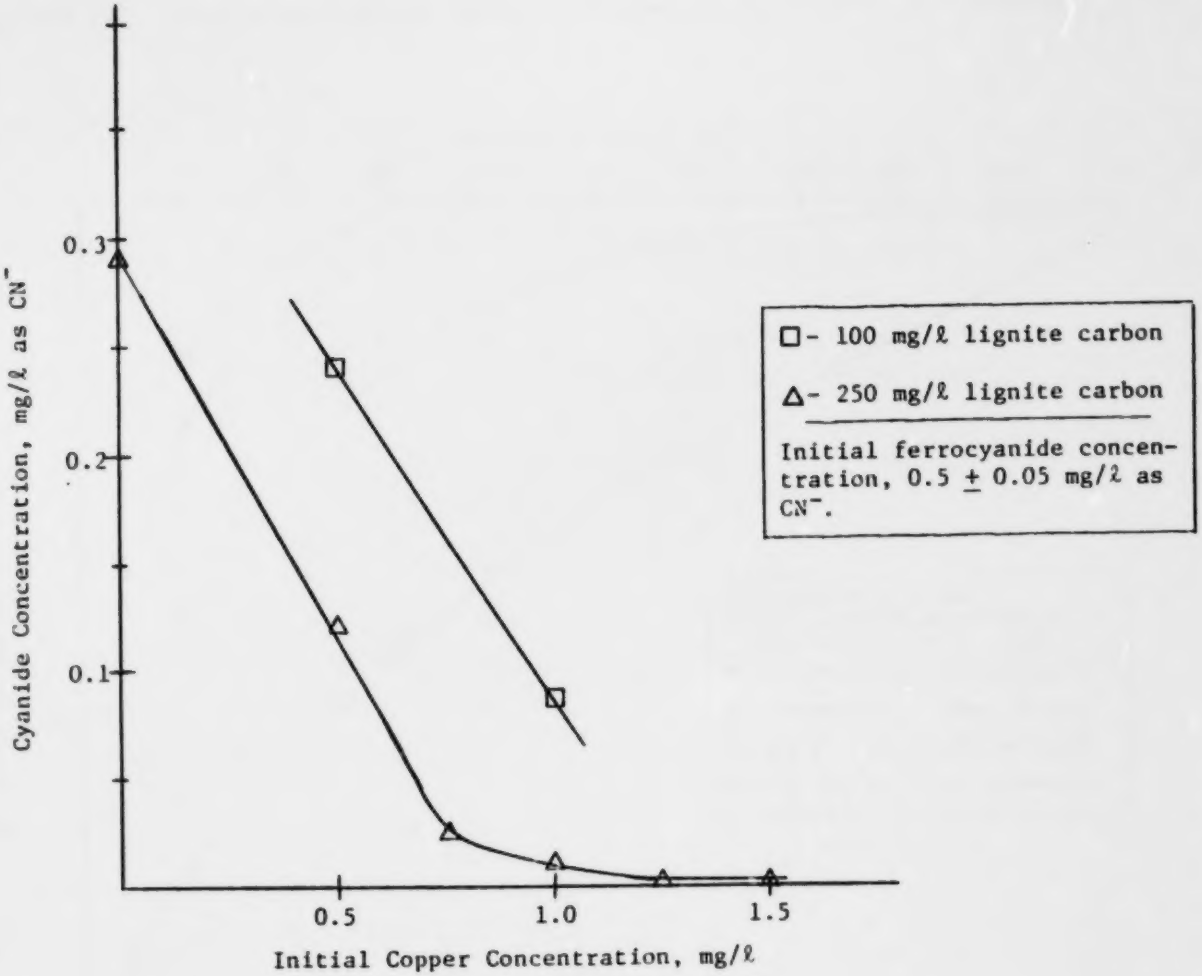


Figure 11. Equilibrium cyanide levels as a function of copper dose.

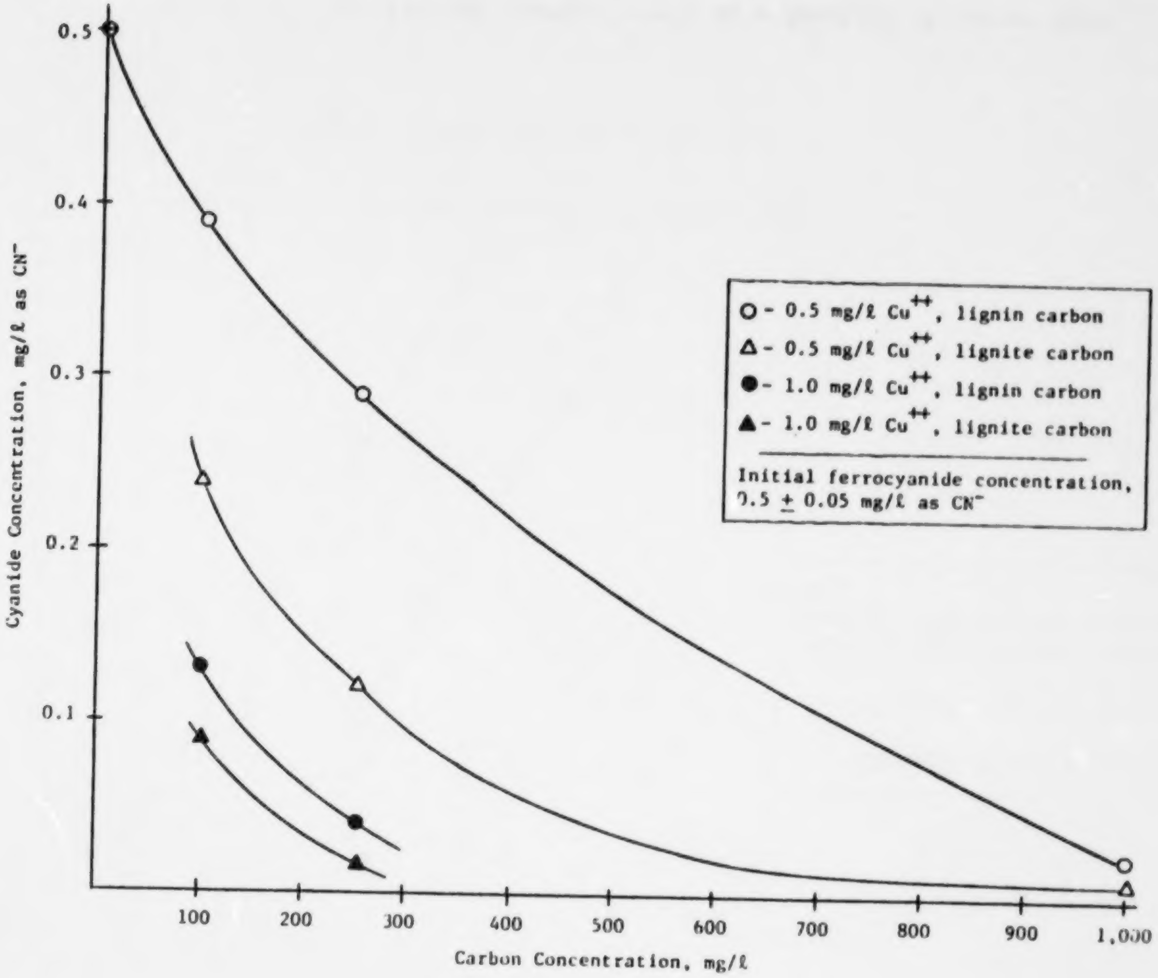


Figure 12. Equilibrium cyanide levels as a function of carbon concentration.

TABLE 7. EFFECT OF CARBON TYPE ON FERRICYANIDE REMOVAL*

Time, hr	Cyanide concentration, mg/ℓ	
	Lignite carbon	Lignin Carbon
0	0.63	0.67
0.25	0.22	0.21
1.0	0.28	0.20
6.0	0.29	0.15
24	0.29	0.11
52	0.28	0.10
72	0.34	0.10

*Copper dosage 1 mg/l
Carbon dosage 250 mg/l

combined since there was not sufficient information to distinguish any difference in copper level for the two carbons. As the carbon dosage increases, as shown in Table 8, the effluent copper level decreases.

TABLE 8. FILTRATE COPPER LEVELS

Initial copper conc., mg/ℓ	Average filtrate copper levels, mg/ℓ		
	100 mg/ℓ carbon	250 mg/ℓ carbon	1,000 mg/ℓ carbon
0.5	0.06	0.05	< 0.02
1.0	0.08	0.05	0.02
1.5	0.19	0.09	---

To maintain a low copper outlet concentration at the 1.0 and 1.5 mg/ℓ inlet copper dosage, higher carbon levels are required. At the 1.5 mg/ℓ copper dosage, the 0.1 mg/ℓ filtrate constraint was exceeded when 100 mg/ℓ carbon was utilized. At the 250 mg/ℓ carbon and 1.5 mg/ℓ initial copper dosage, the average filtrate copper level was below 0.1 mg/ℓ . Thus, to insure compliance with the 0.1 mg/ℓ copper constraint, 1.0 mg/ℓ initial copper was selected as the maximum dosage level. As will be discussed in the following section. 1.0 mg/ℓ copper dosage is also a limitation of this process if it is to be utilized in the biological waste treating units.

COPPER TOXICITY

The concept of introducing a toxic substance (copper) into an activated sludge system to enhance removals of cyanide, at first glance, does not appear to be an acceptable technique for cyanide removal. Supervisors of refinery wastewater treatment plants will need assurance that such a practice will not affect the biological activity in the activated sludge units. Phase II of this study supplies part of this assurance, but a brief review of copper toxicity is provided to delineate the importance and aspects of the toxicity effects of copper.

In the carbon-copper process, a uniform copper dose will be added to the aeration basins; thus, the micro-organisms will become acclimated to the copper level maintained in the system. Acclimation of the micro-organisms to copper was shown to be important in several studies. For example, Sudo and Aiba[16] reported that a copper dosage of 0.25 mg/ℓ copper added to an **unacclimated** culture of protozoa reduced the growth rate by 50%. However, acclimation for 96 hours to the copper increased the concentration at which 50% reduction in growth rate occurred by a factor of 1.2 to 2.2

Poon and Bhayani[17] also investigated the effect of slug doses of copper on both sewage bacteria and the fungus **Geotrichum candidum**. The authors hypothesized that metal toxicity could selectively kill off certain sewage organisms, permitting an overgrowth of poor settling fungus. Poon and Bhayani found that slug doses of copper up to 25 mg/ℓ did not show any obvious toxic effects on the sewage bacteria; however, toxic effects on the fungus were observed from the slug doses. Experiments performed by Lamb and Tollefson[18] indicated that there can be short term impacts. Slug doses of 5 mg/ℓ of copper decreased glucose conversion rates by 75% in the first hour after which recovery occurred. Thus, acclimation of the micro-organisms to copper appears to reduce the manifestations of toxic effects.

The concern in utilizing the PAC-copper system will be the long-term effects of copper addition into an activated sludge unit. Salotto, et al.,[19] found no apparent effect from adding 1 mg/ℓ copper to an activated sludge unit over a 2-1/2 month period. At a continuous feed of 5 mg/ℓ over a six-month period, the authors found the COD removal dropped from 88% (control test) at the high organic loadings to 84%. At low organic loadings, the COD removal efficiency dropped from 86% (control) to 67% with a 5 mg/ℓ copper feed. It was noted in this study that the setteability of the sludge was slightly improved with the copper addition.

A follow-up study by Barth, et al.,[20] concluded that, "one mg/ℓ in the influent sewage is the threshold dose for the aeration phase." An increase in effluent COD values were observed (over the control) when the influent copper level was maintained at 1.2 mg/ℓ for 60 days. This study also reported the biological floc settled rapidly and no bulking was encountered in the metal-fed system, whereas the control units frequently bulked. Anaerobic digestors fed the metal-containing sludge showed no inhibitory effect, even with total copper levels as high as 196 mg/ℓ were measured in the sludge.

Thus, based on the literature, influent copper levels below 1 mg/ℓ should have no noticeable effect on the performance of activated sludge units. In addition, the activated carbon added to the basins should adsorb the bulk of the copper, thus reducing the quantity available to be adsorbed by the biomass. As a limiting constraint for Phase II, 1 mg/ℓ copper was considered the maximum permissible influent dose. Based upon the batch tests reported in Phase I, however, 1 mg/ℓ copper should be sufficient for high levels of cyanide removal.

REGRESSION ANALYSIS

The experimental results obtained in Tests 1 through 12 provided useful data regarding the importance of five operating variables, pH, carbon concentration and type, copper concentration, and mode of copper addition. To quantify the effect of each variable on cyanide removal efficiencies, statistical analyses were performed. Two variables, pH and the mode of copper addition, were ultimately excluded from the statistical analysis. The mode of copper addition did not influence cyanide removal and only a limited number of tests were performed at low and high pH ranges. The data set, which consisted of 23 observations, also limited the number of variables to be tested.

Two cyanide removal mechanisms were hypothesized using the factors controlled during experimentation. These mechanisms are shown below:

$$[CN^-]_e = [C]^{\alpha} \; [Cu]^{\beta} \; [CN]_i^{\gamma} \; [CT] \qquad (1)$$

$$[CN^-]_e = \sigma + \alpha[C] + \beta[Cu] + \gamma[CN]_i + [CT] \qquad (2)$$

where:

$\alpha,\beta,\gamma,\sigma$ = constants

$[C]$ = carbon concentration

$[CN]_i$ = initial cyanide concentration

$[CN]_e$ = equilibrium cyanide concentration

$[Cu]$ = copper concentration

CT = carbon type

Eq 1 indicates that the outlet cyanide concentration is a multiplicative function of the concentrations of inlet cyanide, copper, and carbon, plus carbon type. In Eq 2, a linear relationship is assumed for the range of concentrations considered. Each of these hypotheses was tested using multiple regression techniques. Through statistical analysis, the effect and significance of these operating variables was identified. These results are depicted in Table 9.

The statistical criteria for evaluation were the t-statistic, size of residuals, and adjusted R^2 value. In Table 9, the t-statistic, which is a measure of the significance of the variable, is found below the coefficient in parentheses. For the 23 observations less the number of variables and at the 5% significance level, an approximate t-value of 2.1 indicated a significant variable. As different combinations of variables were considered, the size of the residuals and R^2 factor were monitored. The equation in which the best fit (lowest residuals and highest adjusted R^2) of the data was then identified.

The first six rows of Table 9 illustrate linear relationship regressions of the operating parameters. Line 4 presents the most satisfactory explanation of the effects of operating variables. Line 6 is the same equation as Line 5 in Table 9, but with the dependent variable, the cyanide concentration, at 6 hr. With the exception of Line 6, all of the other regressions utilized the equilibrium cyanide values (average of the 24, 48, and 72 hr. cyanide samples) as the dependent variable. Line 4 presents the most satisfactory explanation of the effects of operating variables. Initial cyanide, carbon, and copper concentrations are very important in determining the equilibrium cyanide concentration. The ensuing equation is a translation of the regression results of Line 4 into operating limitations.

TABLE 9. SUMMARY OF REGRESSION ANALYSES

Dependent Variable	Carbon Conc.	Copper Conc.	Ratio Carbon/Copper	Type of Carbon (dummy)**	Initial [CN⁻]	Log[Carbon]	Log[Copper]	Log[Initial CN⁻]	Constant	Adjusted R^2
1. Equilibrium [CN⁻]	-0.000236 (-2.077)*		1.77×10^{-5} (1.333)						0.178 (4.418)	0.13
2. Equilibrium [CN⁻]	-0.000337 (-3.72)		1.81×10^{-5} (1.89)	-0.0868 (-1.697)	0.6065 (3.080)				-0.0391 (-0.306)	0.56
3. Equilibrium [CN⁻]	-0.000268 (-3.16)		1.51×10^{-5} (1.53)		0.761 (4.16)				-0.194 (-2.05)	0.52
4. Equilibrium [CN⁻]	-0.000305 (-4.83)	-0.150 (-4.93)		-0.0442 (-1.22)	0.703 (5.04)				0.0309 (0.333)	0.78
5. Equilibrium [CN⁻]	-0.000272 (-4.70)	-0.155 (-5.09)			0.779 (6.19)				-0.0423 (-0.589)	0.77
6. Six-hour CN⁻ Equilibrium	-0.000342 (-4.77)	-0.180 (-4.78)			0.843 (5.39)				0.0074 (0.081)	0.74
7. Log [Equilibrium CN⁻]				-0.1116 (-2.35)		-1.558 (-5.018)	-0.403 (-3.12)	2.604 (2.614)	7.9 (4.24)	0.66
8. Log [Equilibrium CN⁻]						-1.353 (-4.078)	-0.363 (-2.55)	3.632 (3.646)	6.79 (3.37)	0.58

* t-statistic shown in ( ).

** Note: The dummy value used for lignite-based carbon was 1 and lignin-based carbon was 0. Coefficients appearing in this column are based on these values.

$$[CN]_e = 0.703[CN]_i - 0.000305[C] - 0.150[Cu] - 0.0442[CT] \quad (3)$$

where:

$[CN]_e$ = equilibrium cyanide concentration, mg/ℓ

$[CN]_i$ = initial cyanide concentration, mg/ℓ

$[C]$ = carbon concentration, mg/ℓ

$[Cu]$ = copper concentration, mg/ℓ

$[CT]$ = carbon type, lignite = 1 and lignin = 0

Eq 3 is expressed as a linear relationship of the operating variables. This equation is appropriate only within the range of initial cyanide concentrations tested (0.3 to 0.7 mg/ℓ) and copper concentrations below 1.5 mg/ℓ. Figures 11 and 12, presented earlier, did show a linear relationship between these separate variables and cyanide over certain concentration ranges.

This analysis has shown that the effect of copper concentration, carbon concentration, and initial cyanide concentration are all statistically significant in influencing the equilibrium cyanide concentration. Carbon type was not demonstrated to be a statistically significant variable at the 5% significance level in the "best fit" equation (No. 4 in Table 9), although the t-statistic for carbon type was significant at the 5% level in Eq 7 and at the 20% level in Eq 2. The limited number of tests with the lignin carbon could account for the lower t-statistic associated with carbon type.

Rows 7 and 8 of Table 9 represent regressions performed assuming a relationship similar to Eq 2. The results of these analyses also support the conclusion that carbon and copper enhance the removal of cyanide. The multiplicative function utilized did not explain as much of the variance in data points as the linear function. This conclusion, however, may be due to the limited range in which each variable was tested.

Implications of these analyses are that by increasing copper and carbon concentrations the cyanide effluent level can be reduced. As pointed out previously, and verified by the size of the coefficients in Table 9, the copper has a stronger influence on the equilibrium cyanide than does carbon concentration. From a economic point of view, this is a favorable result. Doubling the copper dosage (say, from 0.5 to 1.0 mg/ℓ) is more economical than doubling the carbon dosage (say, from 250 mg/ℓ to 500 mg/ℓ), and the resulting reduction in the equilibrium cyanide level is much greater with the copper.

The overall statistical analysis supports the conclusions reached in the previous section. With only 23 sets of data and testing up to five variables, the regression results are significant. To explain 78% of the variation in the results with the tested four variables is a strong implication that the important operating factors have been determined. Especially considering the scatter in the analytical procedure for cyanide, the quantitative results verify the importance of the initial cyanide, copper and carbon concentrations as driving forces.

Included in the Appendix is a summary table of all batch tests performed.

OXIDATION OF CYANIDE ADSORBED ON THE CARBON

In the previous sections, the PAC-copper system was shown to be highly effective in removing cyanide, with removals below 0.01 mg/ℓ achieved from starting solutions containing approximately 0.5 mg/ℓ iron cyanides (as CN^-). The economics of PAC/$CuCl_2$ addition are primarily a function of the carbon requirements. If cyanide is oxidized once adsorbed, then the carbon requirements are reduced and, thus, the economics enhanced. In the background section the oxidation of iron cyanides was reported to occur, but at a slower rate than other complex cyanides.

During approximately half of the batch tests an attempt was made to determine the rate of cyanide oxidation. To analyze for the amount of cyanide remaining on the carbon, the following procedure was used. The carbon samples were obtained by filtration, then resuspended in distilled water and placed in the cyanide distilling flask. After the analysis, the carbon was refiltered, dried, and weighed. The cyanide adsorbed per gram of carbon was recorded. The cyanide remaining in solution (not adsorbed) was also noted. Except for the beginning of each test the amount of cyanide remaining in solution was typically less than 10% of the total cyanide.

The results from these experiments are summarized in Table 10. (The data utilized to develop Table 10 are tabulated in the Appendix.) Assuming a first order decay reaction, the following equation was utilized to determine the cyanide decay rate:

$$C_t = C_o e^{-kt} \qquad (4)$$

where:

C_o is the initial CN^- loading

C_t is the CN^- loading at time t

t is the time in days

k is the decay rate

The decay rate, k, was computed using the least-squares fit procedure for each test. The coefficient of determination, or R^2, was also computed for each test, and these results are included in Table 10. The R^2 coefficients varied considerably from test to test, and the results from four of the tests showed an R^2 value of less than 0.4, indicating considerable scatter in the data. This scatter is attributed primarily to inconsistencies in individual test results and the small sample size. The decay rates ranged from -0.01 to -0.16 day^{-1}, with a mean of -0.06 day^{-1}. If the four tests with R^2 values less than 0.40 are omitted, the recomputed mean decay rate is -0.08 day^{-1}.

TABLE 10. BATCH TESTS - CYANIDE DECAY RESULTS

Test reactor no.	No. of data points	Decay rate(1) (day^{-1})	Intercept(2) (C/Co)	Coefficient of determinations, R^2
1-1	4	-0.06	0.90	0.22*
1-2	4	-0.16	0.96	0.98
1-3	4	-0.12	0.96	0.97
3-1	5	-0.08	0.83	0.44
3-2	6	-0.03	0.97	0.85
4-1	7	-0.01	0.95	0.22*
4-2	5	-0.01	0.96	0.16*
4-3	6	-0.05	0.96	0.87
7-2	3	-0.07	0.97	0.85
7-4	3	-0.08	1.00	0.99
9-2	5	-0.06	0.90	0.70
9-3	6	-0.07	0.96	0.89
9-4	5	-0.02	0.80	0.31*

(1) Based on first order decay; $C_t = Coe^{-kt}$

(2) Intercept is from plotting ln (C/C_o) vs time. For a perfect fit the intercept, $C/C_o = C_o/C_o = 1$

* Coefficient of Determination (R^2) below 0.40

The results of Bernardin,[11] shown in Figure 6, indicated an iron-cyanide decay rate of -0.13 day^{-1}. However, Bernardin was working with an initial concentration of 500 mg/ℓ iron cyanides as compared to the 0.5 mg/ℓ iron cyanide utilized in this study. The thousand-fold difference in starting concentrations could account for the difference in the observed decay rates. Perhaps the most significant finding from these tests is that iron cyanides are destroyed by the PAC/$CuCl_2$ process; however, the rate of decay appears to be slower than that reported by Bernardin.[11]

CONCLUSIONS FROM PHASE I

The primary goal of Phase I was to develop a basic understanding of the chemistry involved in the PAC-copper system for cyanide removal. The results of the regression analysis indicate that this primary goal was achieved.

From the information collected in Phase I, the optimal location in a refinery for treatment of the cyanides was also ascertained. Based upon the findings in Phase I, the logical first choice for cyanide removal would be the biological wastewater treatment (or activated sludge) unit. Cyanide treatment at this location would require little or no capital expenditure, (unless PAC thermal regeneration is desired). The following four possible constraints were identified that could preclude cyanide treatment in the biological units:

1. Cyanide level below 0.1 mg/ℓ may not be achievable because of a concentration-limiting phenomenon.
2. A pH outside the range 6.5 - 8.5 is required for removals of cyanide below 0.1 mg/ℓ.
3. Copper levels in the treated effluent are greater than 0.1 mg/ℓ.
4. The copper levels required for cyanide removal may be high enough to be toxic to the micro-organisms.

These constraints were addressed in the Phase I research. Cyanide removal does not appear to be a concentration-limiting phenomenon. In the batch tests cyanide removals well below 0.1 mg/ℓ were also achieved at the higher carbon and copper dosages investigated. The experimental results also indicated that pH values between 6.5 and 8.5 are satisfactory for cyanide removal. Copper dosages up to 1.0 mg/ℓ were effective in reducing the cyanide to below 0.01 mg/ℓ and yet maintaining effluent (or filtrate) copper levels less than 0.1 mg/ℓ. Copper levels above 1.0 mg/ℓ improved cyanide removal, but effluent copper levels also increased.

The fourth constraint regarding the potential toxic effects of copper on the activated sludge bio-mass was partially answered by the literature review. Confirmation of the copper toxicity literature, however, required the results of Phase II.

SECTION 6

PHASE II - EXPERIMENTAL RESULTS

From the results of the first phase, the PAC/$CuCl_2$ process looked very promising as a cyanide removal technique. There were still many unanswered questions about the process which could not be resolved by batch tests with synthetic wastewaters. Phase II, which utilized a continuous flow biological treatment systems with actual refinery wastewater, was designed to provide information pertaining to the final feasibility of the system.

The Phase I conclusion that the activated sludge system would be the most economical treatment location for the cyanide removal system raised several questions. First, what effect would copper have on the micro-organism? The literature indicated that levels below 1.0 mg/ℓ have little or no effect; however, none of the copper toxicity studies utilized refinery wastes. Another area of concern was the impact of the organics present in the refinery wastewater on the adsorption of the cyanides by carbon. Competitive adsorption between the organics and cyanide for the active carbon sites could potentially reduce the effectiveness of this process to an uneconomical level. Determining the answers to such questions and describing the overall feasibility of the process were established as the goals of Phase II.

In the second phase of laboratory operation, two laboratory scale activated sludge units were set up in parallel. Reactor #1 was utilized as a control reactor; that is, no PAC or $CuCl_2$ was added to this reactor at any time. With the exception of the PAC and $CuCl_2$ addition, the control and test reactors were operated in a like manner. In addition to monitoring the cyanide levels, the following parameters were measured to assess the impact of the PAC/$CuCl_2$ addition on the biological system.

Biochemical Oxygen Demand (BOD_5)
Total Organic Carbon (TOC)
Phenols*
Suspended Solids (SS)
Chemical Oxygen Demand (COD)**

A total of five tests were carried out in Phase II. The first test was designed as a control test, the next three tests evaluated various carbon and copper loadings, and the last test evaluated a two-stage activated sludge process. By investigating the different combinations of PAC and $CuCl_2$ as indicated in the test conditions summary, sufficient data could be generated for determining the feasibility of the process.

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* First part of Phase II only
**Last part of Phase II only

TEST CONDITIONS SUMMARY

Test	Number of Days of Test	Level of $CuCl_2$ Addition* (mg)	Level of PAC Addition* (mg)	Sludge Age
A	21	0	0	12
B	19	0.5	14	12
C	14	0.5	39	15
D	41	1.0	39	15/10
E	12	1.0	25	15

*per liter of feed

Each of the tests is described in detail in the following sections. These experimental results provide a general overview on the applicability and feasibility of the PAC/$CuCl_2$ system.

TEST A - CONTROL TEST

Refinery wastewater feed to Reactors #1 and #2 was initiated on February 8, 1976. Both reactors were initially seeded with approximately 1000 mg/ℓ mixed liquor suspended solids (MLSS). The sludge wastage rate was gradually increased over a 10-day period until the equilibrium wastage rate was attained. The sludge age was then maintined at 12 days in both reactors during Test A.

Test A, initiated on February 19, lasted for a 21-day interval, and Table 11 summarizes the operating performance obtained during this period. As would be expected, the removal performance of both reactors was very similar for all parameters. Phenol removal was very high with an average inlet level of 41 mg/ℓ and all effluent samples below 0.1 mg/ℓ. Cyanide removal was higher than anticipated with an average removal of greater than 90% across both reactors. The only parameter which varied from design was feed throughout. The flow rates of 16.0 and 16.7 l/day for Reactors 1 and 2, respectively, were both below the design 19 l/day because of pump failures on three occasions. As operating experience was gained, the frequency of the pump failures was minimized reducing the fluctuation in flow rates.

Statistical analysis of the experimental data from Test A provided confirmation of the operational similarity of the control and test unit prior to initiation of the test program. The mean cyanide values of the two units were compared using two statistical tools, a t-test and the paired observations. These tests also provided a measure of the comparability of the biological

TABLE 11. TEST A - SUMMARY RESULTS

Parameter	Mean Values			
	Inlet	Effluent Reactor #1	Effluent Reactor #2	Number of Data Points
Flow rate, 1/day	-	16.0 ± 5.0	16.7 ± 4.3	21
Cyanide, mg/ℓ	0.17 ± 0.04	0.016 ± 0.021	0.014 ± 0.016	14
BOD, mg/ℓ	250 ± 120	13 ± 5	14 ± 10	16
TOC, mg/ℓ	111	27	31	10
Phenol, mg/ℓ	41	<0.10	<0.10	4
Copper, mg/ℓ	<0.02	<0.02	<0.02	8
Suspended Solids, mg/ℓ	25	22	21	11

The purpose of Test A was to demonstrate that the two reactors performed in a similar manner prior to beginning the carbon/copper addition tests.

Sludge age - 12 days, both reactors
Length of test - 21 days (after an 11 day start-up period)
Carbon dosage - None to either reactor
Cupric Chloride dosage - None to either reactor

activity of the two units. The first statistical test was comparing the cyanide levels of Reactors 1 and 2. The following t-test was used for the paired observation tests:

$$T = \frac{M_D - E(M_D)}{\text{est } \sigma_{M_D}} \qquad (5)$$

where:

T = is the 't' statistic with n-1 degrees of freedom

n = is the sample size

$M_D = \frac{\Sigma(Y_{i_1} - Y_{i_2})}{n}$

Y_{i_1} = Observed value of the ith sample from reactor 1

$E(M_D)$ = Expected difference in population means

est σ_{M_D} = unbiased standard deviation of M_D

With the aid of this test, various hypotheses were formulated and the confidence levels of rejection and/or acceptance determined. Using the 10% confidence level for rejecting the hypothesis, the similarity of the two units was tested. The statistical results from Test A for cyanide and BOD_5 removals are presented in Table 12. Statistical analyses were limited to the cyanide and BOD results because of the small number of samples for the other parameters. However, from Table 12, the results indicate that the effluent cyanide and BOD levels from the two reactors are indeed very similar. Thus, even though there was wide dispersion around each sample mean, the performance of the two reactors was considered to be the same based upon the statistical analysis.

TEST B - LOW CARBON/LOW COPPER TEST

The first test for evaluating the PAC/$CuCl_2$ system utilized a low carbon and copper dose. Then, in subsequent tests the carbon and/or copper dosages could be increased and the new test initiated quickly. This technique minimized the time interval between tests since several complete turnovers of solids would be necessary to flush high concentrations out of the system.

Cyanide removal through just a biological system was shown to be greater than 90% in Test A. Therefore, the apparent cyanide loading on the activated carbon was expected to be quite small. Apparent loading used in this context is considered the difference in cyanide removed between the control and test unit divided by the carbon dosage. A copper dose of 0.5 mg as Cu per liter of feed was selected for Test B accompanied by a carbon dose of 14 mg per

TABLE 12. TEST A - STATISTICAL RESULTS

Parameter	Sample means mg/ℓ		Hypothesis	'T' Statistic	Hypothesis is accepted or rejected
	M_1	M_2			
Effluent Cyanide levels	0.0158	0.0139	$M_1 = M_2$	0.45	Accepted
Effluent BOD_5 levels	13.4	14.2	$M_1 = M_2$	0.63	Accepted

Paired observations and 10% significance level utilized.

TABLE 13. TEST B - SUMMARY RESULTS

Parameter	Inlet	Effluent reactor #1-Control	Effluent reactor #2-Test	Number of data Points
Flow rate, 1/day	-	17.9 ± 3.8	18.4 ± 2.8	19
Cyanide, mg/ℓ	0.31 ± 0.13	0.017 ± 0.010	0.020 ± 0.010	19
BOD, mg/ℓ	180 ± 180	16 ± 11	30 ± 13	13
TOC, mg/ℓ	145	24	25	8
Phenol, mg/ℓ	57	<0.10	<0.10	6
Copper, mg/ℓ	<0.02	<0.02	0.15	8
Suspended solids, mg/ℓ	26	8	15	9

Sludge age - 12 days, both reactors
Length of test - 19 days (at start of test, slugged dosed the aeration basin of reactor #2 with 2.5 gm Carbon plus 9.5 mg Cu.)
Carbon dosage - Reactor #2 only - 14 mg/ℓ
Cupric Chloride - Reactor #2 only - 0.5 mg as Cu/ℓ dosage

liter of feed. The sludge age was maintained at 12 days, thus allowing a theoretical PAC concentration of approximately 250 mg/ℓ in the aeration basin of the test reactor.

At the beginning of Test B, the test reactor (#2) was slug-dosed with 2,500 mg of carbon (lignite type) and 9.5 mg of copper to bring the operating conditions close to the design levels. Test B was then carried out over a 19 day period. A summary of performance results during Test B is presented in Table 12. The BOD_5 removal across the test reactor was 89% as compared to 94% for the control reactor. The difference in BOD_5 removal efficiency was attributed to the initial slug-dose of copper and perhaps carbon. The BOD_5 removal dropped off the first day in the test unit and never recovered during this test interval. In retrospect, the carbon and copper should have been added gradually over several days so as to not upset the system.

The results of Test B didnot indicate any substantial advantage of the test unit over the control. Cyanide removal across the test reactor averaged 93.5% as compared to 94.5% across the control unit. Comparing the total quantity of cyanide removed across both reactors (taking into account the slightly different flow rates), yields of 5.34 mg/day for the test unit and 5.24 mg/day for the control unit were obtained. Thus, the apparent loading on the carbon was the following:

$$\frac{5.34\ \frac{\text{mg CN}^-}{\text{day}} - 5.24\ \frac{\text{mg CN}^-}{\text{day}}}{0.250\ \frac{\text{gm Carbon}}{\text{day}}} = \frac{0.37\ \text{mg CN}^-}{\text{gm Carbon}} \qquad (6)$$

This apparent loading was quite low when compared to the batch test loadings of typically 1.5 - 2.0 mg CN^-/gm Carbon. The results from Test B indicate that because of the competitive adsorption between the organics and the cyanide for the active carbon sites greater quantitites of PAC would be required to satisfactorily remove the cyanides.

By comparing the effluents from the two reactors in a statistical manner, the effect of the $PAC/CuCl_2$ system can be determined. In Table 14 the statistical test results are summarized. The cyanide removal efficiency of the control and test unit appears to be the same in this test. The means are close together, and allowing for the standard deviation and analytical precision these means cannot be considered distinctive. Thus, on a statistical basis, no additional cyanide removal could be attributed to the $PAC/CuCl_2$ addition. The slug dose of copper did significantly reduce biological activity, and in Table 14 the mean effluent BOD from the control is significantly better at the 10% confidence level. Thus, toxic effects of copper occurred when copper amounts were slug-dosed and the biological system did not recover.

TEST C - HIGH CARBON/LOW COPPER TEST

The results of Test B suggested that a higher carbon dosage would be necessary to improve the cyanide removal. At the end of Test B, the carbon dosage was increased from 250 mg/day to 750 mg/day, or an average of 39 mg carbon per liter of wastewater. The sludge age was also increased from 12 days to 15

TABLE 14. TEST B - STATISTICAL RESULTS

Parameter	Sample mean, mg/ℓ M_1	M_2	Hypothesis	'T' Statistic	Hypothesis is accepted or rejected
Effluent Cyanide levels	0.0167	0.0196	$M_1 = M_2$	-1.65	Accepted
Effluent BOD levels	16.5	30.1	$M_1 = M_2$	5.85	Rejected

Paired observations and 10% significance level utilized.

days to allow a longer holding time for cyanide oxidation on the carbon. This resulted in an equilibrium carbon level in the aeration basin of approximately 1000 mg/ℓ for Test C. After a 2-day period for acclimation of the system to the higher carbon make-up rate, Test C was initiated and continued for a 14-day period.

The results of Test C are summarized in Table 15. Unlike the previous test, no detrimental effects on the organic removal (BOD and TOC) were observed in the test reactor. The mean effluent copper level was also lower in Test C (0.10 mg/ℓ) as compared to Test B (0.15 mg/ℓ), and this was considered the result of the higher carbon level in Test C. The PAC/$CuCl_2$ addition reduced the mean effluent cyanide level over the control unit by 0.019 mg/ℓ, or 28%. The apparent cyanide loading for Test C is computed below:

$$\frac{11.63\ \frac{\text{mg CN}^-}{\text{day}} - 11.39\ \frac{\text{mg CN}^-}{\text{day}}}{0.750\ \frac{\text{gm Carbon}}{\text{day}}} = \frac{0.32\ \text{mg CN}^-}{\text{gm Carbon}} \tag{7}$$

This apparent loading is lower than the 0.37 mg CN^-/gm carbon determined for Test B, as would be expected. (Removal efficiency increases as the loading on carbon decreases in a completely mixed system.) As compared to the loadings reported in the batch tests (1.5 - 2.0 mg CN^-/gm carbon), the loading in Test C indicates that competitive adsorption by the organics is a real phenomenon that consumes most of the active sites on the carbon. However, sufficient carbon was available for the removal of an additional 0.019 mg/ℓ cyanide over the control reactor.

The statistical analyses confirm the influence of the PAC/$CuCl_2$ addition. In Table 16 the computed statistical results are summarized. That the PAC/$CuCl_2$ system improved cyanide removal over the control can be stated at the 2% significance level. At the 10% significance level, the effluent cyanide was reduced at least an incremental 0.01 mg/ℓ due to the addition of the PAC/$CuCl_2$. Thus, the increase in carbon concentration improved the cyanide removal.

Linear regression analyses were performed for the test and control units, comparing the effluent cyanide level to the inlet cyanide concentration. The results from both the test and control reactors were combined, and a dummy variable utilized for the use of carbon/$CuCl_2$. The following equation is the result of this technique.

$$\begin{array}{llll} [\text{Effluent CN}^-] = & 0.14\ [\text{Inlet CN}^-] & -\ 0.019\ [\text{PAC}] & \\ \text{T-Statistic} & (2.84) & (-2.81) & (8) \end{array}$$

where:

PAC = 1 for test reactor

= 0 for control reactor

TABLE 15. TEST C - SUMMARY TABLE

Parameter	Inlet	Effluent Reactor #1	Effluent Reactor #2
Flow rate, 1/day	-	19.2 ± 3.8	19.0 ± 3.7
Cyanide, mg/ℓ	0.66 ± 0.071	0.067 ± 0.024	0.048 ± 0.016
BOD, mg/ℓ	380 ± 90	27 ± 9	28 ± 7
TOC, mg/ℓ	130	27	26
Phenol, mg/ℓ	80	<0.10	<0.10
Copper, mg/ℓ	<0.02	<0.02	0.10
Suspended solids, mg/ℓ	10	10	10

Sludge age - 15 days
Length of test - 14 days (after a 2 day transition from Test B)
Carbon dosage - Reactor #2 only - 39 mg/ℓ
Cupric chloride dosage - Reactor #2 only - 0.5 mg as Cu/ℓ

TABLE 16. TEST C - STATISTICAL RESULTS

Parameter	Sample means, mg/ℓ M_1	M_2	Hypothesis	'T' Statistic	Hypothesis is accepted or rejected
Effluent Cyanide levels	0.0670	0.0478	$M_1 = M_2$	3.01	Rejected
Effluent Cyanide levels	0.0670	0.0478	$M_2 + 0.011 \leq M_1$	1.28	Accepted
Effluent BCD levels	26.7	27.6	$M_1 = M_2$	-0.408	Accepted

Paired observations and 10% significance level utilized.

Both parameters, the inlet cyanide concentrations and the presence of the PAC/$CuCl_2$ are significant factors at the 1% level. The R^2 (adjusted) for this regression was 0.34, which indicates that there are other variables not included in this regression that influence effluent cyanide concentration, and these other variables are discussed in a latter section. Basically, this statistical regression illustrates the importance of PAC/$CuCl_2$ in removing cyanide, holding all other operational variables constant.

The significance of the PAC/$CuCl_2$ is depicted graphically in Figure 13. The lines are separated by the difference in the effluent cyanide means, 0.019 mg/ℓ which is the most probable difference. Because of the use of the dummy variable to indicate the effects of PAC/$CuCl_2$, the lines in Figure 13 are parallel. Not enough data were collected to discern the true relative slopes of the two lines; although carbon adsorption theory would predict that the lines would converge at the lower inlet cyanide concentrations.

The various statistical analyses of the results from Test C clearly show that the addition of PAC and $CuCl_2$ into a biological wastewater treatment system significantly improves cyanide removal. The results also indicate that there was no deterioration in the removal of other organics (as measured by the BOD and TOC tests) as a result of the PAC/$CuCl_2$ addition. The average cyanide removal of 28% over the control reactor was achieved with a relatively high carbon level and a low copper level. In the following test, the copper dose was increased to ascertain if cyanide removal could be further enhanced via more copper.

TEST D - HIGH CARBON/HIGH COPPER TEST

The final test with the single stage activated sludge units utilized a high carbon and copper dosage to determine the long term effects of the PAC/$CuCl_2$ addition. The copper level for this test was increased to 1.0 mg/ℓ for a feed rate of 19 mg of copper per day. The carbon level was maintained at the same level as the previous test, 750 mg per day for a dosage of 38 mg of carbon per liter of wastewater.

The transition from Test C to Test D was accomplished by allowing the test reactor to adjust to the higher copper feed rate for one day. After this acclimation period Test D was initiated and lasted for 43 days. Any potential detrimental effects of PAC/$CuCl_2$ addition to the activated sludge system were expected to be evident by the end of the 43-day test.

During the first 30 days of Test D the sludge age was maintained at 15 days after which it was reduced to 10 days for the remainder of the test. The reason for the change in sludge age is included with the results.

In Test C with the lower copper dose, the PAC/$CuCl_2$ addition reduced the mean cyanide effluent level by 28% over the control. In Test D the copper dose was double that utilized in Test C, which based upon the batch tests, should have resulted in effluent cyanide levels over 50% lower than the control reactor. The results of Test D, summarized in Table 12, show that the test reactor effluent cyanide level averaged only 9% lower than the control

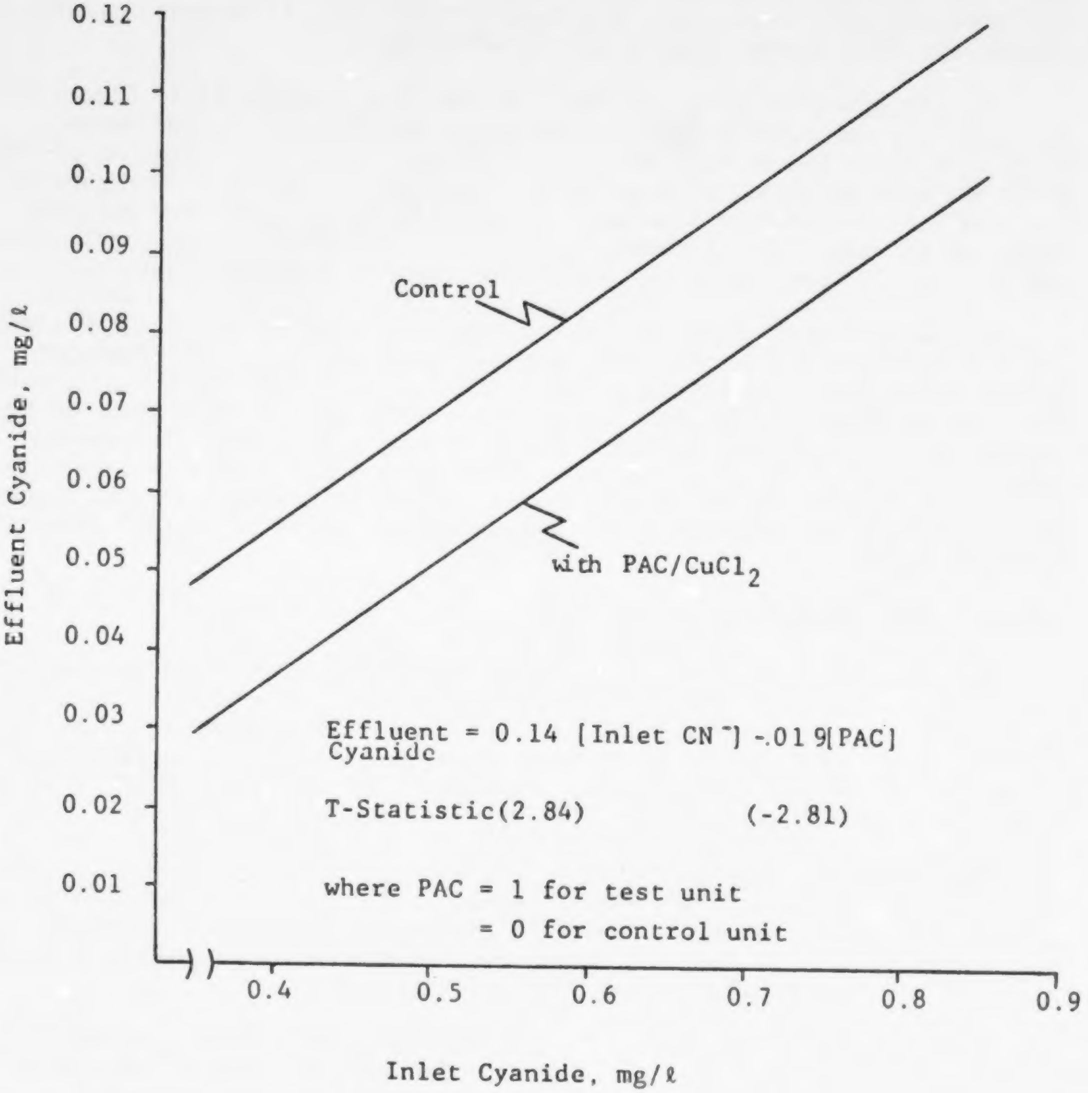


Figure 13. Test C-Predicted effect of PAC on effluent cyanide levels.

reactor during the 43 day test. In addition to the cyanide removal being lower than expected, the dampening effect observed in Test C in the effluent cyanide variation as a result of the carbon addition was not apparent in this test. The standard deviation of the test unit effluent cyanide level during Test C was 0.016 mg/ℓ as compared to 0.024 mg/ℓ in the control reactor. In Test D, the standard deviations were 0.051 and 0.034 mg/ℓ for the test unit and control unit effluent cyanide levels, respectively. Frequency distributions for the effluent cyanide levels, shown in Figure 14, also reflect this greater variation in the test units's effluent.

Also contained in the summary Table 17 are the other chemical characteristics used to describe the effluent and monitored during Test D. The BOD removal was improved by the addition of PAC/$CuCl_2$ by 26% over the control unit. This effect on BOD removal is graphically depicted in Figure 15. The larger mean effluent COD and TOC concentration from the test reactor could be attributed to the carbon fines in the effluent, as all of the analyses were performed on unfiltered samples. The removal of over 99% of the phenol across both reactors continued as in previous tests.

The test reactor effluent copper level averaged 0.20 mg/ℓ indicating that 80% of the copper was being adsorbed onto the carbon and removed from the system in the waste sludge.

Cyanide Removal Performance

Analysis of the effluent cyanide concentrations from the two reactors indicate that twice during Test D major performance changes occurred in the test reactor. These changes in operating performance divide Test D into 3 intervals, which for discussion purposes, are designated D1, D2, and D3.

The change in effluent cyanide concentration with time is presented for the test and control reactor in Figure 16. Interestingly enough the inlet cyanide concentrations illustrated in Figure 17 do not indicate this variation from period to period. The effluent characteristics of the reactors in Test D are depicted by time intervals in Table 18, and the performance in each interval is discussed herein.

The first phase, D1, lasted for 16 days, during which time the control reactor effluent cyanide averaged 0.073 mg/ℓ compared to 0.045 mg/ℓ for the test reactor. The PAC/$CuCl_2$ addition thus resulted in a mean cyanide level 38% lower than the control reactor during the first 16 days of Test D. The 17th day of the test marked the beginning of a 2 week period during which the test reactor performed poorly compared to the control unit. The control unit effluent during this second phase, D2, averaged 18% less cyanide with a mean effluent cyanide concentration of 0.115 mg/ℓ while the test unit averaged 0.140 mg/ℓ. After 30 days the sludge wastage rate was increased (sludge age decreased) in an attempt to reduce the cyanide equilibrium concentration in solution by lowering the total quantity of cyanide maintained in the aeration tank.

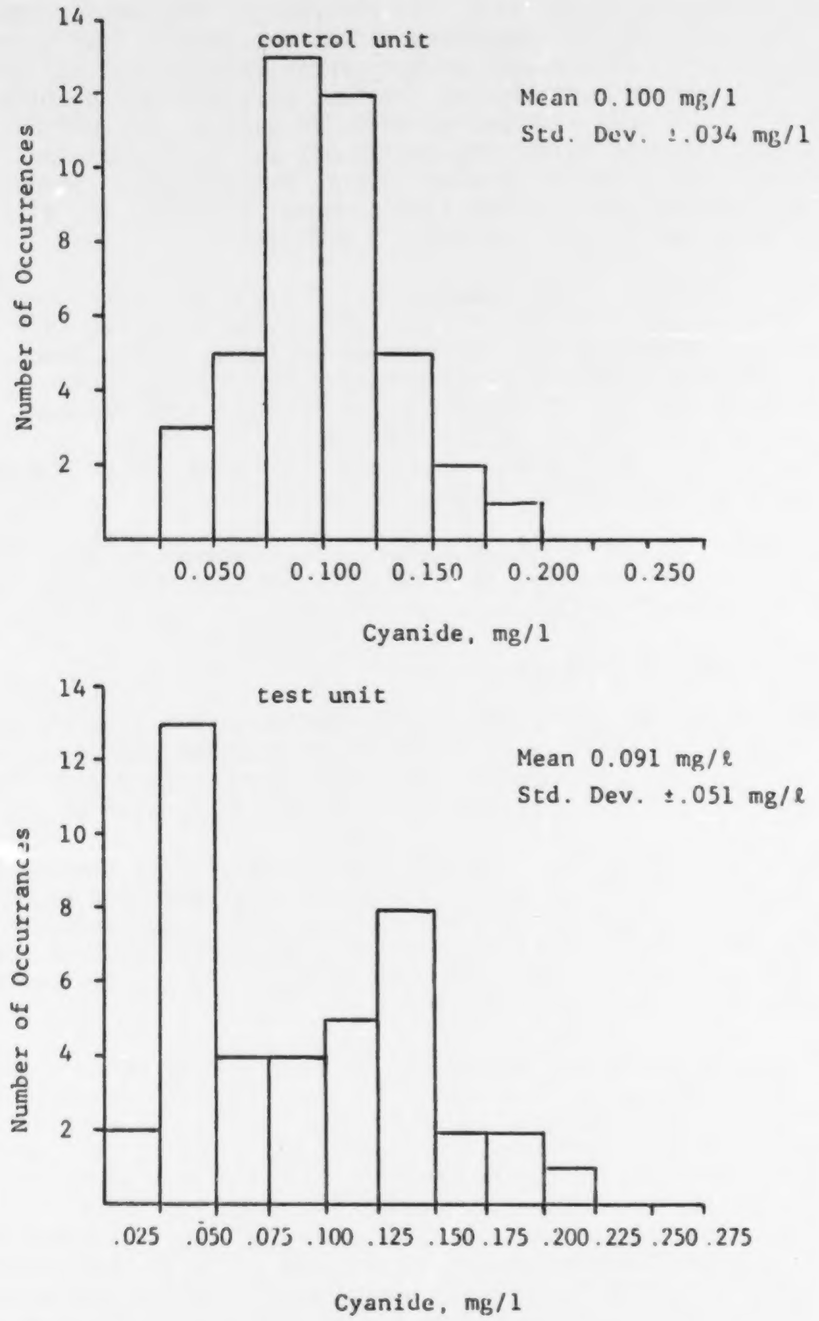


Figure 14. Test D-Cyanide frequency distributions.

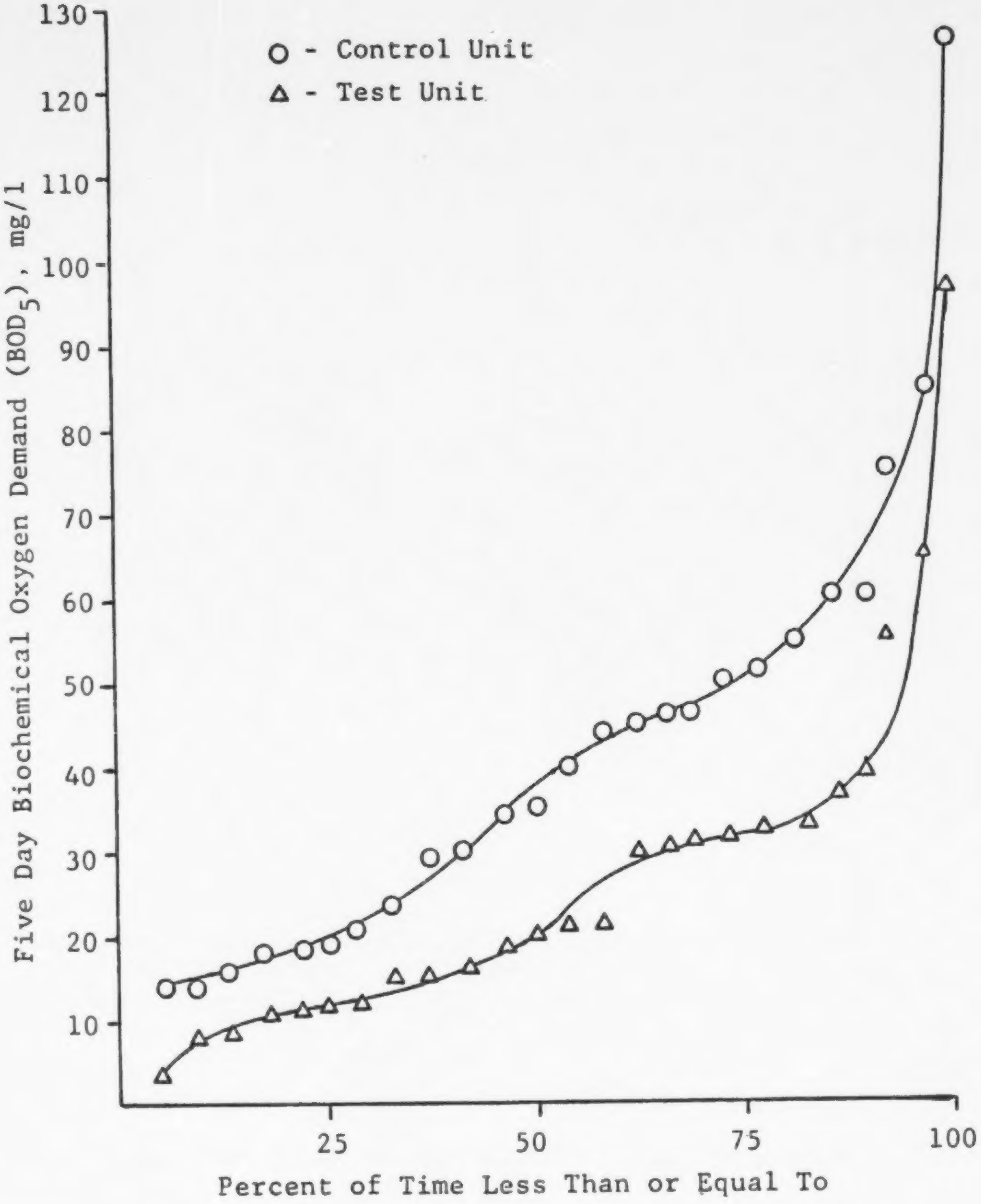


Figure 15. Effect of powdered carbon on BOD_5 removal-Test D.

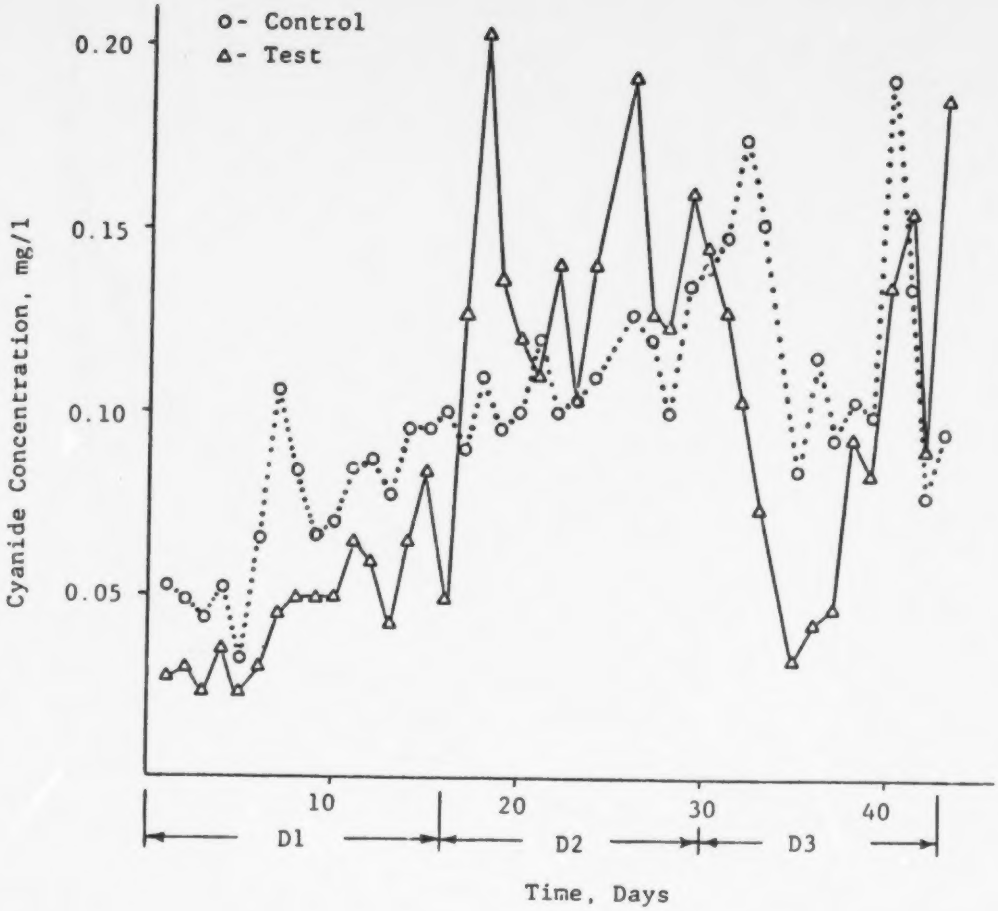


Figure 16. Test D-Effluent cyanide levels with time.

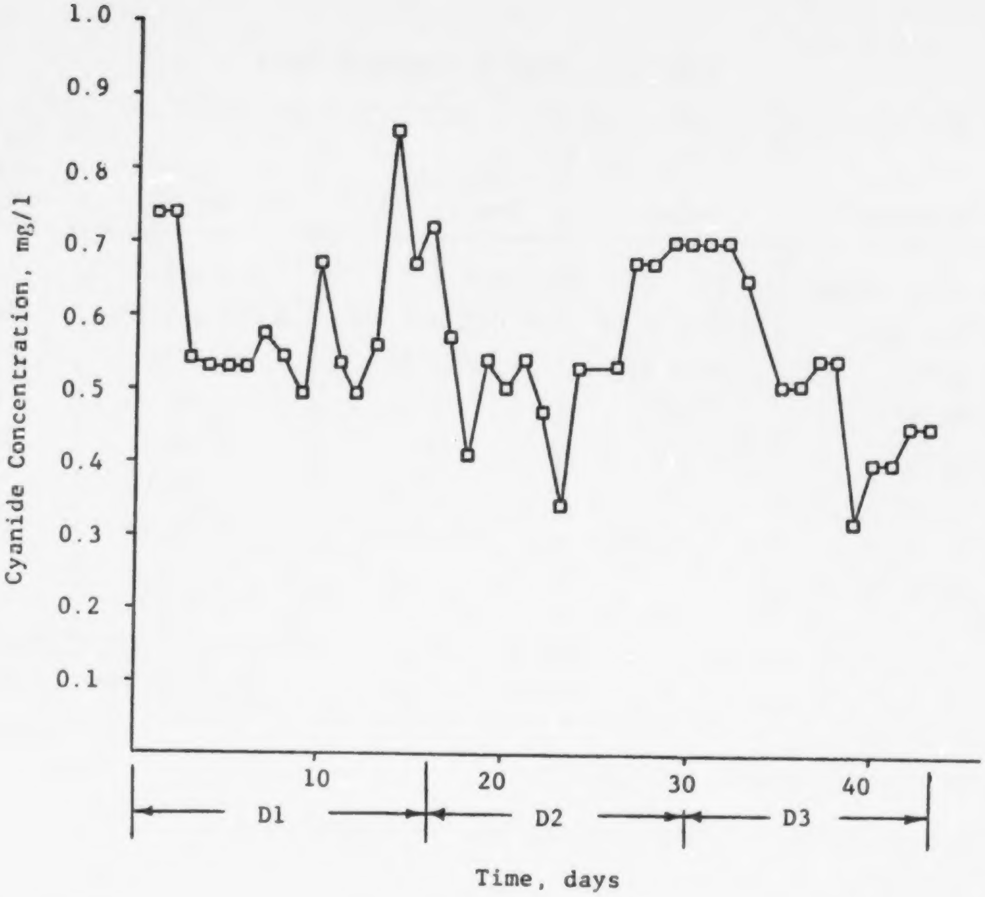


Figure 17. Test D-Inlet cyanide level with time.

TABLE 17. TEST D - SUMMARY TABLE

Parameter	Inlet	Effluent reactor #1	Effluent reactor #2	Number of Samples
Flow rate, l/day	-	19.4 ± 2.2	19.5 ± 2.3	41
Cyanide, mg/ℓ	0.56 ± 0.12	0.100 ± 0.034	0.091 ± 0.051	41
BOD, mg/ℓ	280 ± 110	38 ± 20	28 ± 21	23
COD, mg/ℓ[1]	262	70	84	9
TOC, mg/ℓ	111	24	29	17
Phenol, mg/ℓ	71	<0.10	<0.10	4
Copper, mg/ℓ	<0.02	<0.02	0.20	19
Suspended solids, mg/ℓ	24	10 ± 3	13.5 ± 10	19

Sludge Age - 15 days for first 30 days, sludge age 10 days for last 13 days
Length of Test - 43 days (after a 1 day transition from Test C)
Carbon dosage - Reactor #2 only - 38 mg/ℓ
Cupric Chloride dosage - Reactor #2 only - 1.0 mg as Cu

[1] COD samples taken only during the last 18 days of Test D.

TABLE 18. TEST D - BY PERIODS - SUMMARY TABLE

#1 - Days #1-16, Sludge Age - 15 days

Parameter	Inlet	Effluent reactor #1	Effluent reactor #2	Number of samples
Cyanide, mg/ℓ	0.61 ± 0.11	0.073 ± 0.022	0.045 ± 0.017	16
BOD, mg/ℓ	330	34	34	9
TOC, mg/ℓ	106	24	23	5
Suspended solids, mg/ℓ	13	10	9	7

#2 - Days #17-31, Sludge Age - 15 days

Parameter	Inlet	Effluent reactor #1	Effluent reactor #2	Number of samples
Cyanide, mg/ℓ	0.56 ± 0.11	0.115 ± 0.018	0.140 ± 0.028	15
BOD, mg/ℓ	270	37	15	9
TOC, mg/ℓ	141	28	38	7
Suspended solids, mg/ℓ	22	10	22	6

#3 - Days #32-43, Sludge Age - 10 days

Parameter	Inlet	Effluent reactor #1	Effluent reactor #2	Number of samples
Cyanide, mg/ℓ	0.51 ± 0.11	0.123 ± 0.038	0.097 ± 0.048	11
BOD, mg/ℓ	220	49	40	5
TOC, mg/ℓ	74	19	21	5
Suspended solids, mg/ℓ	38	27	12	6

After 31 days the test reactor effluent cyanide concentration decreased rapidly and remained lower than the control for the remainder of the test. During this period, D3, the test reactor effluent cyanide level averaged 0.097 mg/ℓ and the control unit averaged 0.123 mg/ℓ for a 26% improvement attributed to the PAC/$CuCl_2$. Frequency distributions of the effluent cyanide concentrations for the three phases of Test D are illustrated in Figure 18. The frequency distributions in Figure 18 show the increasing effluent cyanide concentration from the control unit with time. (This same trend was also observed in Figure 16.) An analysis of these phenomena is discussed later in this section.

BOD Removal Performance

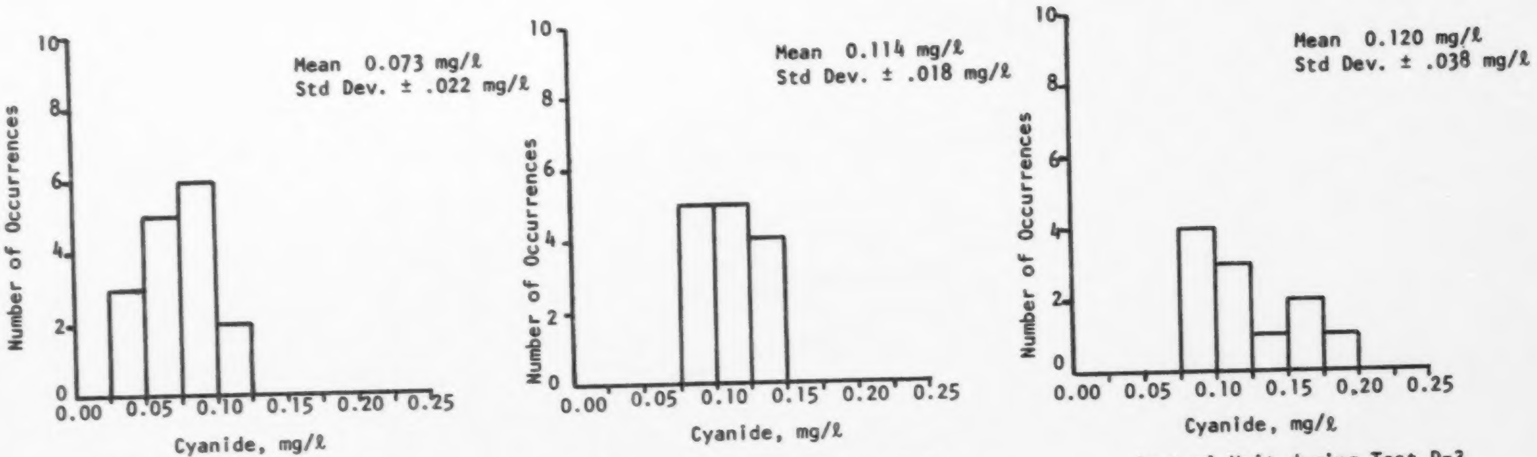
During Test D the BOD level was also monitored in the inlet and both effluents. The variation in the BOD concentrations with time are presented in Figures 19 and 20 for the effluents and inlet, respectively. The first phase consisted of steadily rising BOD's in the effluents whereas the inlet BOD was actually dropping during this period. After the first 10 days of the test the inlet BOD concentration rapidly increased but due to analytical difficulties (contaminated dilution water), no BOD data for the last 6 days of this period were obtained.

Although the BOD data are extremely limited near the end of D1, and the beginning of D2, Figure 20 indicates that the organic loading was considerably higher than during the rest of Test D. A higher organic loading could result in the displacement of some adsorbed cyanide on the carbon due to the higher driving force of the organics. While the data are too limited to draw any conclusions concerning the reason for the higher cyanide levels from the test reactor during D2, the higher organic loading during the later portion of D1 is a plausible explanation. One other interesting observations from Figure 19 is the lower effluent BOD's during period D2 in the test reactor effluent. Whether this is related to the higher effluent cyanide levels during the same period could not be determined. Although the test reactor effluent BOD was significantly lower than the control reactor during period D2, (59% lower), the total organic carbon results did not exhibit the same trend. The TOC results are presented in Figure 21.

Statistical Analysis

The statistical analyses of Test D for each time period are summarized in Table 19. The effluent cyanide concentrations for all of Test D were significantly lower in the test reactor than in the control reactor and so were the effluent BOD levels. To further clarify the results of Test D statistical analyses of the results during each period were also performed, as summarized in Table 19.

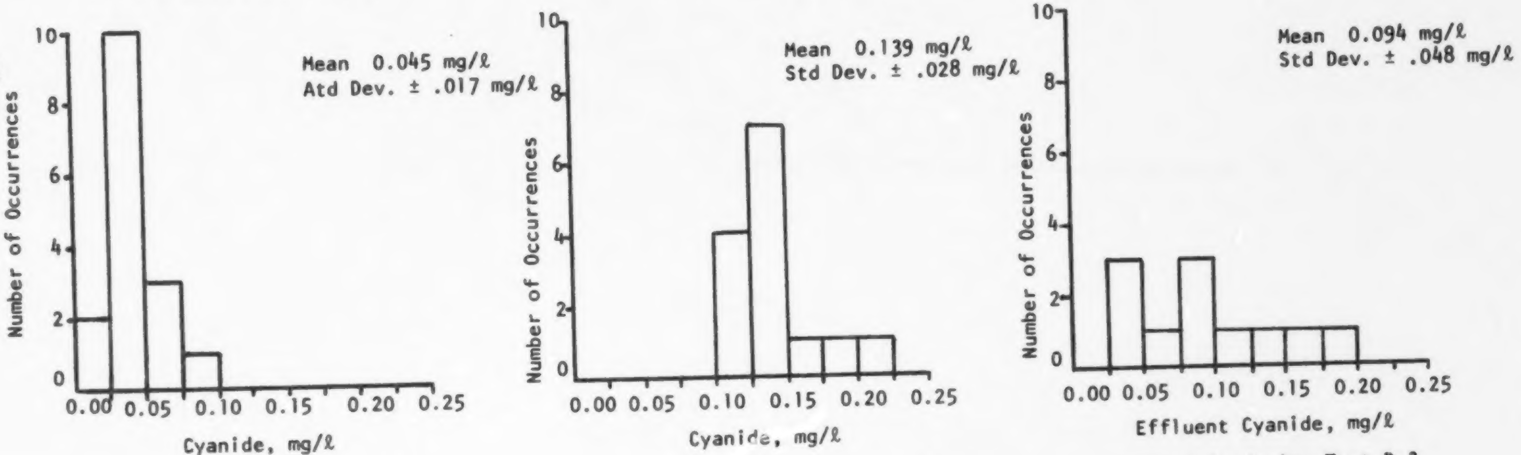
During period D1, the effluent cyanide level from the test reactor was consistently lower than the control, and this difference in performance was verified statistically at the 10% significance level. In period D2 an increase in the test unit's effluent cyanide level occurred which resulted in higher cyanide concentrations for the test unit rather than the control.



Control Unit during Test D-1

Control Unit during Test D-2

Control Unit during Test D-3



Test Unit during Test D-1

Test Unit during Test D-2

Test Unit during Test D-3

Figure 18. Test D - Cyanide frequency distributions by period.

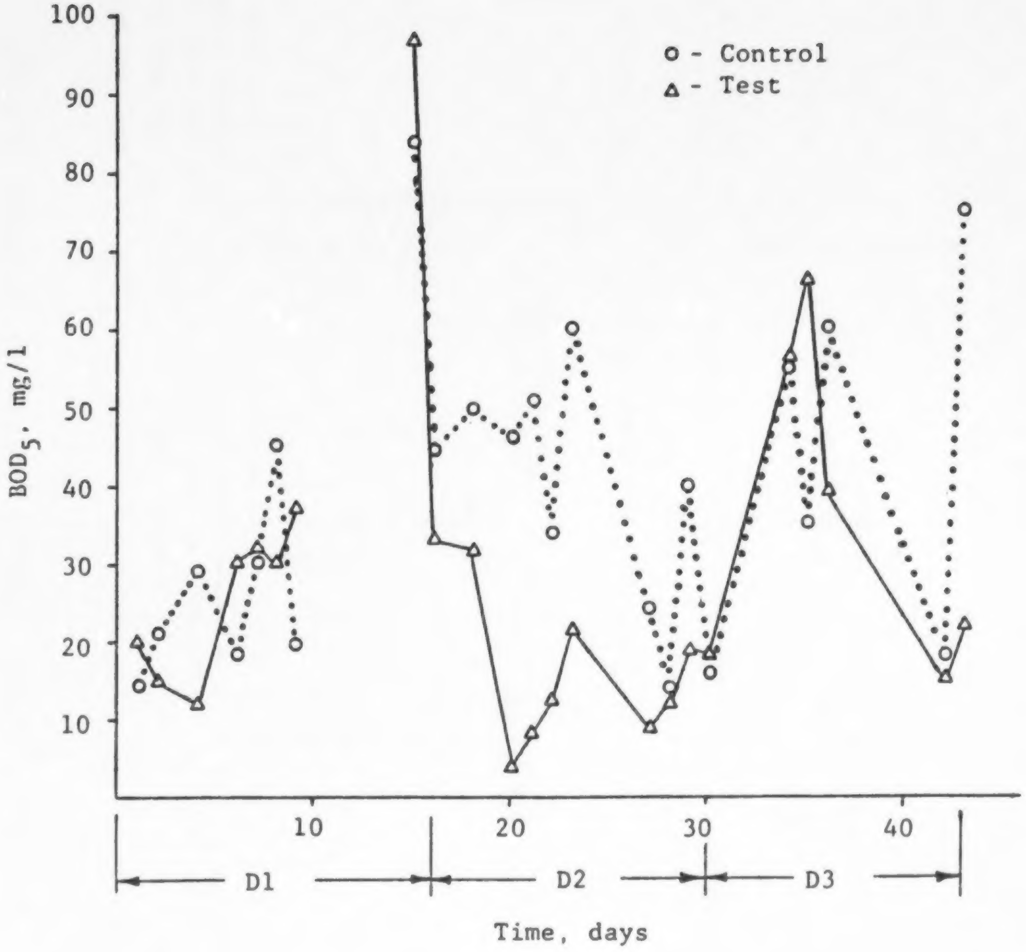


Figure 19. Test D-Effleunt BOD_5 with time.

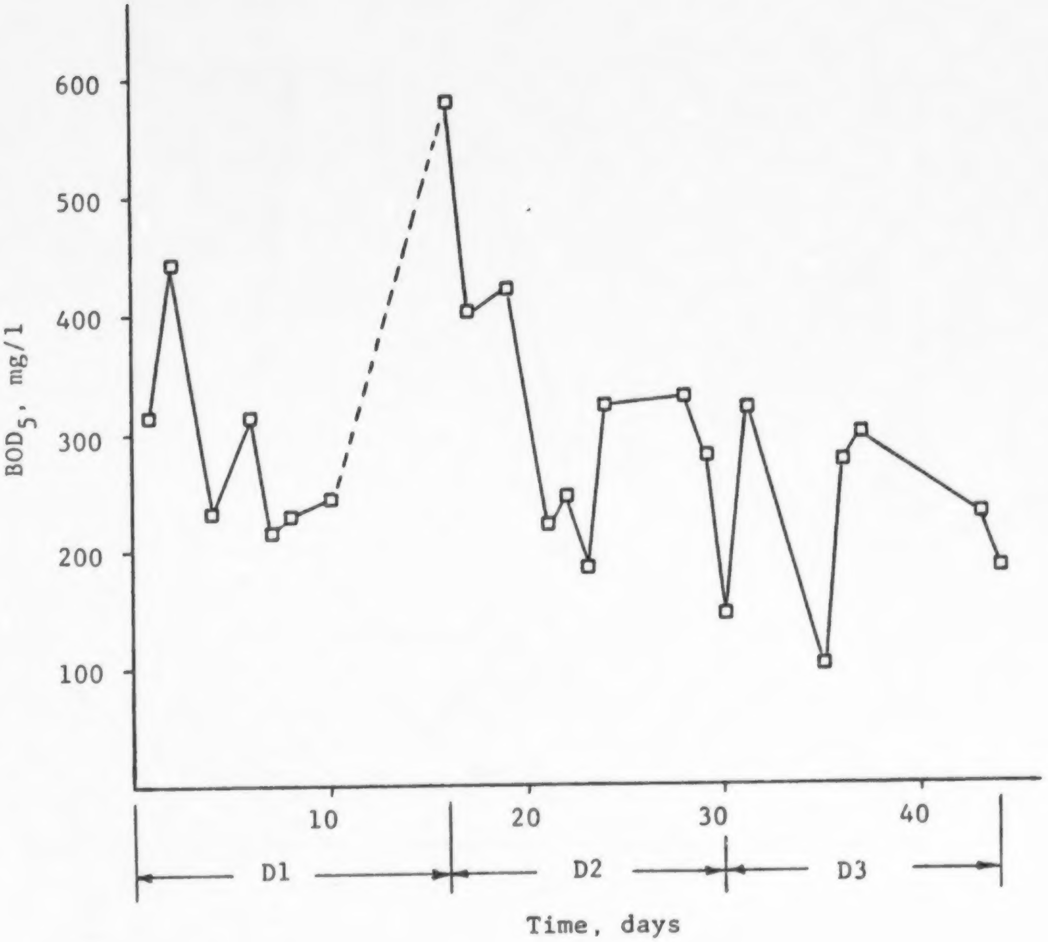


Figure 20. Test D-Inlet BOD$_5$ with time.

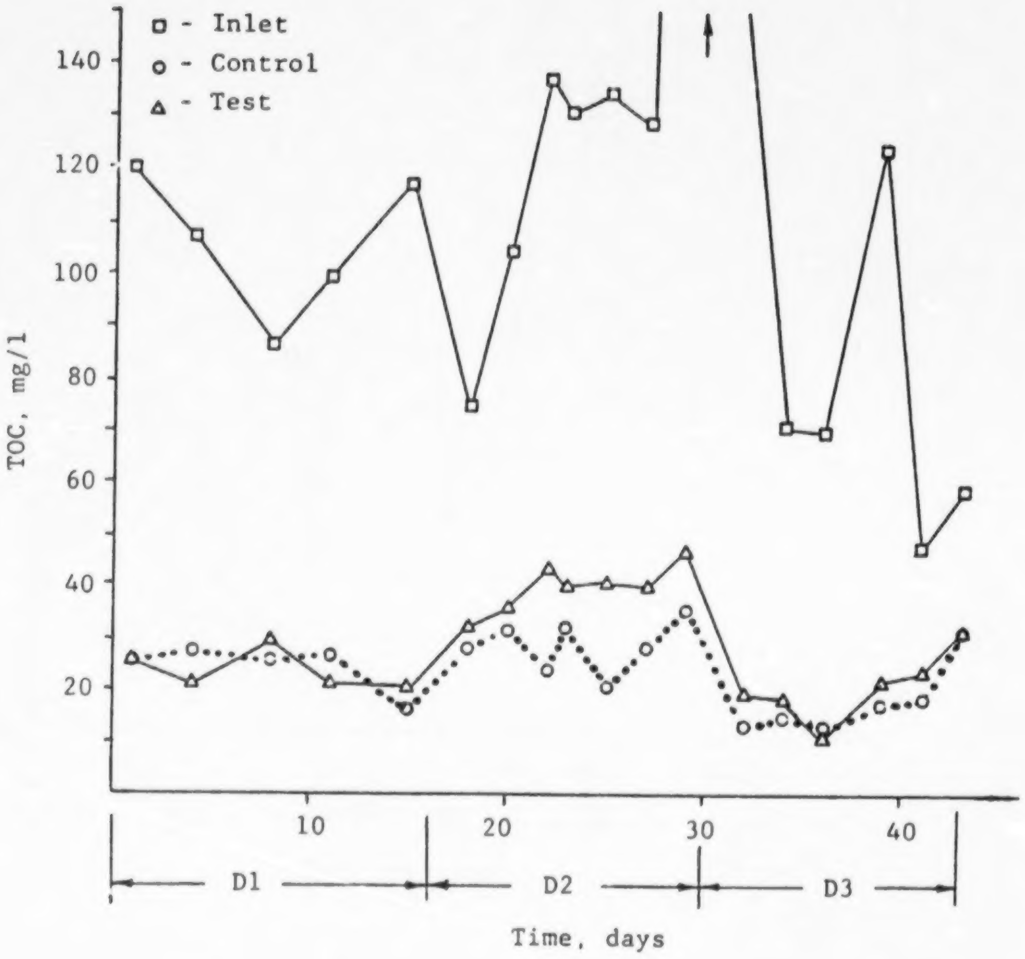


Figure 21. Test D-Inlet and effluent TOC with time.

TABLE 19. TEST D - STATISTICAL RESULTS

Parameter	Sample means, mg/ℓ M_1	M_2	Hypothesis	'T' Statistic	Hypothesis is accepted or rejected
Effluent Cyanide - D	0.0997	0.0905	$M_1 = M_2$	2.29	Rejected
Effluent BOD - D	38.3	27.6	$M_1 = M_2$	2.45	Rejected
Effluent Cyanide D-1	0.0726	0.0452	$M_1 = M_2$	7.85	Rejected
Effluent Cyanide D-1	0.0726	0.0452	$M_2 + 0.023 \leq M_1$	1.25	Accepted
Effluent Cyanide D-2	0.1142	0.1392	$M_1 = M_2$	-2.50	Rejected
Effluent Cyanide D-3	0.122	0.097	$M_2 = M_1$	4.41	Rejected

Paired observations and 10% significance level utilized.

The performance difference was statistically analyzed and the two means were significantly different at the 10% level. During the last test interval, D3, the removal efficiencies of the two reactors reversed again with the better performance being achieved in the test unit. The statistical test used indicated that this performance change was significant at the 10% level.

Thus, it can be confirmed with some statistical support that there occurred significant differences in performance both between the two units, and between the different time periods. However it should be noted that the sample dispersion and sample size both influence the validity of the conclusions offered and should be considered limitations to the analysis.

Discussion of Test D

The phenomenon of decreasing removal efficiency was one which was observed not only in Test D but throughout the continuous tests. The control reactor exhibited a generally decreasing cyanide removal efficiency during the course of these tests as summarized below in Table 20.

TABLE 20. CYANIDE REMOVAL ACROSS THE CONTROL REACTOR

Test	Mean inlet cyanide concentration, mg/ℓ	% Cyanide removed
A	0.17	91
B	0.31	94
C	0.66	90
D1	0.61	88
D2	0.56	80
D3	0.50	76

A satisfactory explanation for the decreasing removal efficiency in the control could not be readily determined. The change with time could be attributed to a gradually increasing fraction of complex cyanides in the feed. The possibility of an increasing fraction of complex cyanides in the refinery wastewater arises due to the greater demand for gasoline during the summer months. As the summer approaches, refineries generally increase their feed rates and cracking severity in the cracking units. The very severe cracking conditions promote the formation of more cyanide. The more cyanide produced, the more corrosion that will occur, and this in turn effects the quantity of iron cyanide generated. The sour water stripper removes all but a small fraction of the simple cyanides (stripping appears to be a concentration limiting phonomena) and none of the iron cyanides. Thus, one would expect a relatively constant simple cyanide concentration in refinery wastewaters and increased complex cyanide concentration during periods of maximum gasoline production. Iron cyanide removals across biological treatment systems are lower than the simple cyanide removals, as discussed in Section 3. The postulated higher complex cyanide concentrations would explain the reduced cyanide removal efficiency across the control reactor observed with time.

The increasing percentage of complex cyanides in the inlet would also have an effect on the test unit due to the difference in rates of oxidation of simple and complex cyanides. As explained in Section 3, the rate of oxidation of complex cyanides has been found to be much slower than for simple cyanides. Thus, the test unit would be affected by an increasing equilibrium cyanide concentration in the carbon sytem. As the fraction of complex cyanides in inlet increased, so would the amount adsorbed onto the carbon, but due to the slower oxidation rate, more cyanide adsorbed on the carbon would in turn increase the equilibrium cyanide concentration remaining in solution or in the effluent.

A comparison of the apparent cyanide loadings on the PAC for the various tests is shown in Table 21. This loading, which is defined as the difference between the quantity of cyanide removed in the test and control units divided by the carbon dosage, changed significantly during the test program. The apparent loading at the beginning of Test D was more than 2½ times greater than that for Test C, even though the carbon dose and inlet cyanide concentration were approximately the same. (The copper dosage for Test D was twice that of Test C, and this accounts for the greater removal and thus higher apparent loading.) However, the apparent cyanide loading for Test D1 was still below the 1.5 to 2.0 mg CN^-/gm carbon measured in the batch tests.

TABLE 21. APPARENT CARBON LOADINGS

Test	Carbon dose, mg/ℓ	Apparent loading, mg CN^-/gm carbon
B	14	0.37
C	39	0.32
D1	38	0.80
D2	38	(-0.59)
D3	38	0.73

The results of Test D confirm the findings of the previous continuous tests, that is, competitive adsorption from the organics reduces the quantity of cyanide adsorbed by the PAC/$CuCl_2$ addition. The higher outlet cyanide levels during period D2 were attributed to overloading of the carbon from high organic levels in the feed, although the data are lacking to confirm this statement. To increase the quantity of cyanide removed, the following two options are available:

1. Reduce the organic loadings
2. Increase the carbon dosage.

The economics of this process depend almost entirely on the carbon dosage. Instead of increasing the carbon dosage further, the first option of a reduced organic loading was evaluated in the final test. Some refineries utilize a two-stage biological treatment scheme. By adding the PAC/$CuCl_2$ to the second-stage, the organic loading on the carbon should be 50-80% lower than in a one-stage system. In the last continuous test, Test E, a two-stage biological treatment system was utilized to check the hypothesis that a lower organic loading should increase the quantity of cyanide removed.

TEST E - LOWER ORGANIC LOADING WITH MEDIUM CARBON/HIGH COPPER DOSAGE

In order to evaluate the effect of lower organic loadings on cyanide removal, a two-stage activated sludge system was used in Test E. The effluent from a common first stage was split into two streams; one for a second-stage control and the other a second-stage test reactor. In the second-stage test reactor a carbon dose of 25 mg/ℓ, or 500 mg/day, and a copper level of 1.0 mg/ℓ or 19 mg (as Cu) per day were utilized. The carbon and copper were both added for twelve days prior to initiating Test E to acclimate the micro-organisms and to build up the carbon level in the aeration basin.

The actual test period lasted 12 days at a sludge age of 15 days. As in the previous tests, the efficiency of the biological treatment process was monitored by measuring the BOD, COD, and TOC levels in the influent and effluents. The average performance characteristics of the test and control reactors are summarized in Table 22.

As Table 22 indicates, the effluent cyanide concentration from the test reactor was 53% lower than that of the control reactor. The effluent cyanide level from the control reactor averaged 0.141 mg/ℓ, as compared to the mean inlet cyanide level of 0.140 mg/ℓ. The lack of any cyanide removal across the second stage control reactor supports the previous hypothesis that primarily simple cyanides are removed in the first stage activated sludge unit, leaving the stable complex cyanides for the second stage. As in Test C and part of Test D, the carbon addition dampened the day to day cyanide variation as measured by the standard deviation, (0.024 mg/ℓ to 0.060 mg/ℓ). This dampening effect in the effluent cyanide level is also evident in Figure 22, which compares the two effluent cyanide levels with respect to time.

The biological performances of the second-stage control and test reactor also varied but to a much smaller extent. The organic loading on the second-stage, which averaged 82 mg/ℓ BOD (unfiltered), 92 mg/ℓ COD (filtered), and 25 mg/ TOC (filtered), was much lower than that for Tests A, B, C, and D. The effluent from the test reactor contained, on the average, less BOD (6 mg/ℓ), COD (7 mg/ℓ), and TOC (1 mg/ℓ) than the effluent from the control reactor. However, the suspended solids in the test effluent were usually 5 mg/ℓ higher than the control effluent.

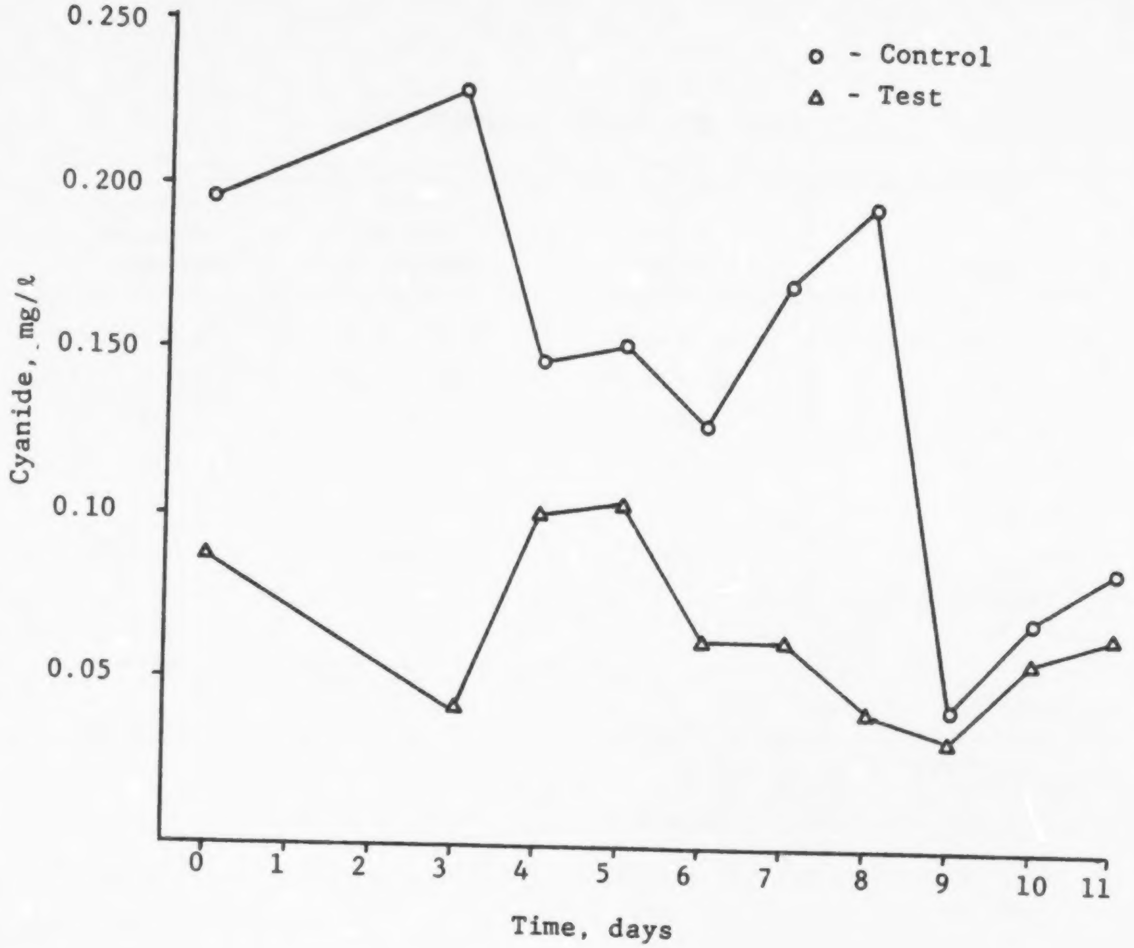


Figure 22. Test E-Effluent cyanide levels with time.

TABLE 22. TEST E - SUMMARY TABLE

Parameter	Inlet	Test effluent Reactor #3	Control effluent Reactor #4
Flow rate, ℓ/day	---	20.0 ± 1.9	20.2 ± 3.6
Cyanide, mg/ℓ	0.140 ± 0.045	0.066 ± 0.024	0.141 ± 0.060
BOD, mg/ℓ	82	21	27
COD, mg/ℓ(1)	92	43	50
TOC, mg/ℓ(1)	25	10	11
Copper	<0.02	0.20	<0.02
Suspended solids, mg/ℓ	---	17	12

Sludge age - 15 days
Length of test - 12 days (after a 12 day acclimation period with carbon and copper added to system).
Carbon dosage - Reactor #3 only - 25 mg/ℓ
Cupric chloride dosage - Reactor #3 only 1.0 mg as Cu/ℓ

(1)For Test E only all COD and TOC analyses were performed on filtered samples.

Only a limited amount of data was collected during this short test, and to statistically evaluate the results, these data were pooled using a dummy variable for reactor type. With 20 data points the difference in cyanide removal efficiencies between reactors was considered statistically significant at the 0.5% level. Or, in other words, the probability that the control and test reactor performed differently is greater than 0.995. This can be observed visually by inspecting Figure 23. Not only are the means quite different but also the dispersion and location of the frequency distribution.

The large reduction in cyanide (53%) attributed to the PAC/$CuCl_2$ addition tends to support the hypothesis that a lower organic loading would increase the removal of cyanide. The apparent cyanide loading (the difference in quantity of cyanide removed by the test and control reactors, divided by the carbon dose) for Test E was 2.74 mg CN^- per gm carbon. The apparent cyanide loadings for all the one-stage tests ranged from 0.32 to 0.80 mg CN^- per gram of carbon (see Table 21). Such a variation in cyanide loading clearly indicates that lower organic loadings increased the quantity of cyanide removed per gram of carbon.

SUMMARY OF PHASE II

Continuous tests were performed over a four-month period to evaluate PAC/$CuCl_2$ addition into an activated sludge system for cyanide removal. Batch tests, utilizing iron cyanides added to Chicago tap water, achieved cyanide removals in excess of 95%. The continuous tests were performed with actual refinery wastewaters utilizing two reactors; one as a control unit and the other for evaluating the PAC/$CuCl_2$ system. A series of five tests were performed, which are listed below:

Test A - no carbon - no copper
Test B - low carbon - low copper
Test C - high carbon - low copper
Test D - high carbon - high copper
Test E - medium carbon - high copper (two-stage system)

The results from these five tests demonstrated that activated sludge units remove as much as 90% of the cyanide present in refinery wastewaters. The addition of PAC/$CuCl_2$ directly into the aeration basin can remove additional quantities of cyanide without any apparent effect on the micro-organisms. With the exception of the initial slug dose in Test B, no inhibitory effects on the biota were observed in the activated sludge performance.

The addition of PAC may improve the removals of BOD, COD, and TOC. While a significant improvement in BOD removal was observed in the longest test (Test D) as a result of the PAC addition, Tests B and C did not confirm this trend and the data in Test E were too limited for analysis. The TOC and COD analysis were performed on unfiltered samples (except in Test E) and the carbon fines in the effluent samples contributed to both the COD and TOC values observed. Again in Test E, the data were too limiting to make any definite statement regarding the removals of COD and TOC.

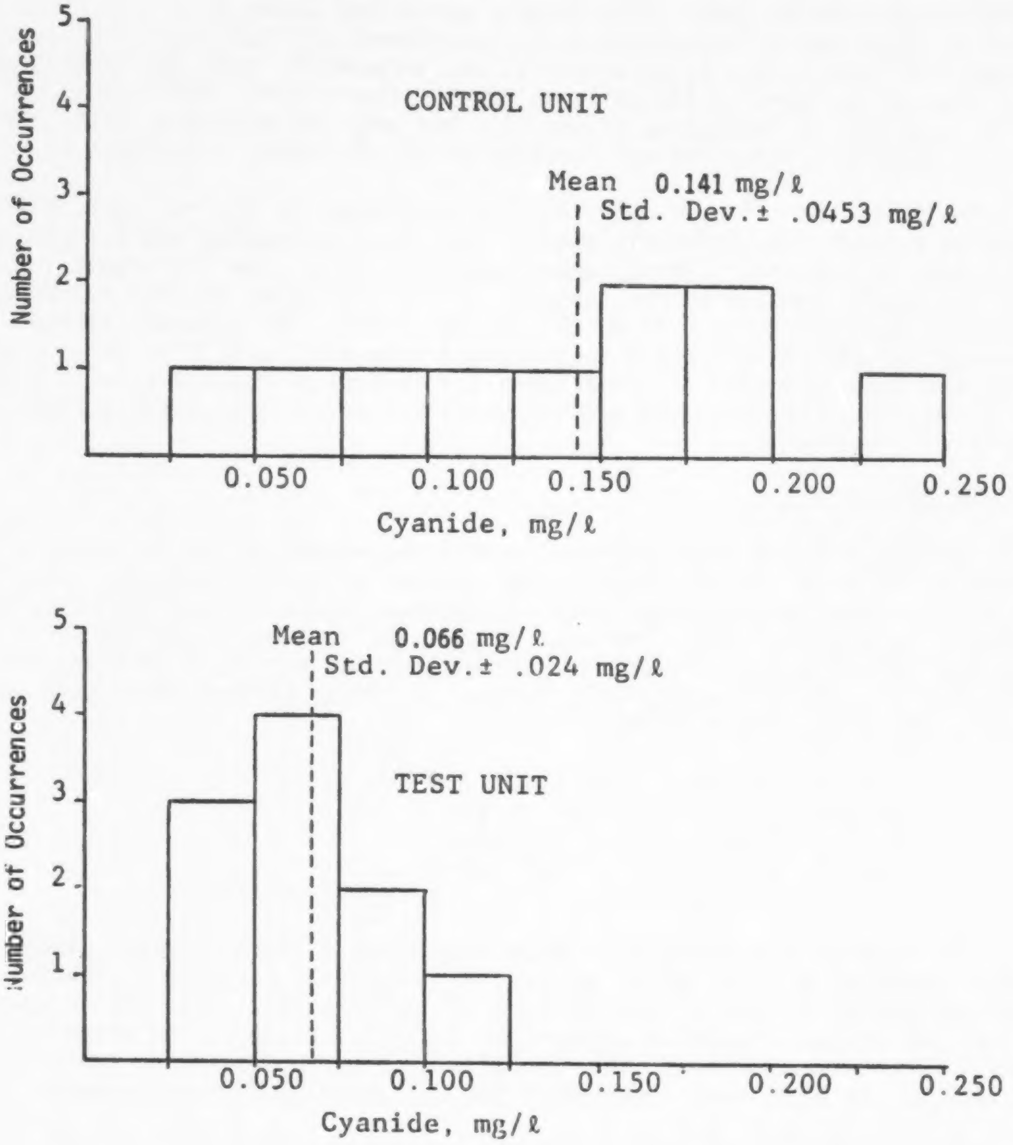


Figure 23. Test E-Effluent cyanide frequency distribution.

The organic loading was found to be a major factor in the removal of cyanide by the PAC/$CuCl_2$ system. Test E supported the hypothesis reached after Test D, namely, decreasing the organic loading improves the cyanide removal efficiency. This is probably due to the effect of reducing the competition between the smaller amount of organics and the cyanide for the available adsorption sites on the carbon. The increased availability of adsorption sites to cyanide resulted in more cyanide being adsorbed and, therefore, corresponding higher apparent cyanide loadings. The greater apparent cyanide loading of 2.74 mg CN^- per gm of carbon, is a more efficient use of the carbon, thereby decreasing costs for the system. Therefore, the use of the PAC/$CuCl_2$ system is most attractive in a low organic load waste stream, such as in the second-stage of a two-stage activated sludge system.

SECTION 7

ECONOMIC IMPLICATIONS OF THE PAC/$CuCl_2$ SYSTEM

The technological feasibility of utilizing the PAC/$CuCl_2$ system in an activated sludge unit to remove cyanides has been demonstrated by the results of Phase II experimentaion. Reduction of cyanides can be achieved; however, the competitive adsorption of organic compounds on the activated carbon reduces the quantity of cyanide adsorbed per gram of carbon. Without preferential adsorption of the cyanides, this system will require larger carbon dosages when the organic concentration is high.

Cost estimates for operating this PAC/$CuCl_2$ system in a refinery provide additional insight on its overall feasibility and applicability. Based on the data collected from the continuous tests in Phase II, which most nearly simulated actual refinery conditions, operating conditions of a PAC/$CuCl_2$ system are projected. The costs of operating and installing such a system are then developed for single-stage and two-stage activated sludge units. A comparison of these costs with that of a granular carbon system emphasizes the economic advantages derived from the PAC/$CuCl_2$ treatment technique. Thus, the operating range of economic feasibility is clearly demonstrated for this experiment.

OPERATING CRITERIA FOR PAC/$CuCl_2$ SYSTEMS

The continuous tests of Phase II provided basic information regarding the operating performance of a PAC/$CuCl_2$ cyanide removal system. Important criteria in designing a system or estimating costs are the apparent cyanide loading, existing effluent cyanide level, and copper dosage required. Data gathered experimentally were used to describe these factors.

To determine the quantity of carbon required to remove a specified amount of cyanide, the apparent loading must be estimated. The apparent cyanide loading is defined as the difference in cyanide removed between the test and control reactors, divided by the carbon dosage. According to adsorption theory, the loading of a contaminant on carbon decreases as the carbon dosage increases. Or, in other words, for each additional increment of carbon added, a progressively smaller increment of the contaminant will be removed. (This can be readily seen in the batch test results, as shown previously in Figure 12.)

To ascertain the effect of carbon dosage on apparent loading Tests B and C were both run at a constant copper dosage. The apparent loadings for Tests B and C, plotted in Figure 24, illustrates the effect of carbon dosage.

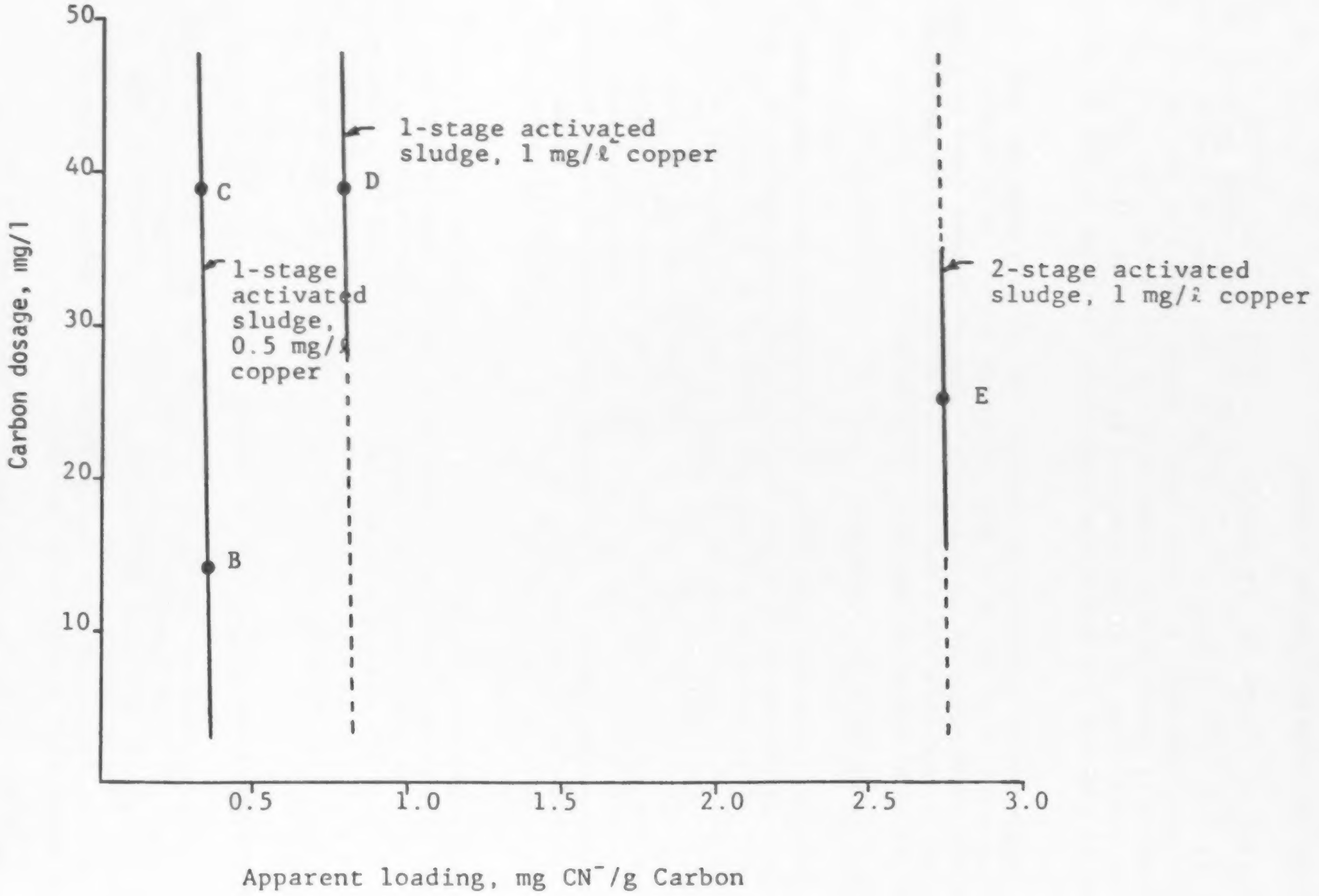


Figure 24. Effect of carbon dose on apparent loading.

From Figure 24, increased carbon dosage had only a slightly negative influence on the apparent cyanide loading.

Also shown in Figure 24, are extrapolated loading lines for the conditions utilized in Test D and E, under the assumption that these lines would be parallel to the line passing through Test B and C. The apparent cyanide loading is only slightly dependent on carbon levels, which means that the quantity of cyanide removed is approximately proportional to the carbon dose. Using Figure 24, the quantitites of carbon required to achieve specified effluent levels can be computed for both a one-stage and a two-stage activated sludge system.

The copper concentration to be used in a PAC/$CuCl_2$ system was specified at 1 mg/ℓ as a result of the batch and continuous tests. No detrimental effect on the performance of the activated sludge units were found at 1 mg/ℓ copper; however, the literature indicates that above 1 mg/ℓ, the performance of the activated sludge units may begin to decrease.

COST ESTIMATION OF PAC/$CuCl_2$ SYSTEMS

The costs of utilizing a PAC/$CuCl_2$ cyanide removal system were based upon the apparent loading values of Figure 24 and copper concentration of 1 mg/ℓ with the goal of achieving an effluent cyanide level of 0.025 mg/ℓ. In Table 23 the chemical costs are presented for single-stage and two-stage activated sludge units. The chemical costs were developed under the assumption that the PAC would not be recovered after use. By eliminating PAC regeneration, this cyanide treatment method can be applied without any capital expenditure or additional plant operators. For larger carbon users regeneration would be more practical and economical. Thus, the estimated chemical costs presented Table 23 are actually close to the total cost of this system. Powdered carbon is the primary cost of the system (85-95%). Thus the required carbon dose determines the economic feasibility of the system.

While the PAC/$CuCl_2$ process will not solve the cyanide problem for all refineries, this process has considerable potential for some refineries. For refineries with two-stage activated sludge units operated in series, the costs as shown in Table 23, are approximately one-fourth of those for a single-stage system. To place the costs of operation of this proposed cyanide removal system in perspective, a comparision with another potential system is made in the following section.

COST COMPARISION OF PAC VS GAC CYANIDE REMOVAL SYSTEMS

The cost advantages of the PAC/$CuCl_2$ system are most aptly illustrated by comparison with other cyanide treatment methods. As stated in Section 3, all existing cyanide treatment methods are considered expensive by the refining industry. The economics of this cyanide treatment system are compared with the GAC catalytic oxidation system described in Section 3 as an example of the projected cost savings to be realized.

The GAC/$CuCl_2$ system was investigated by one refinery in Illinois.[12] Utilizing the refinery cost estimates and cyanide levels, a cost comparison

TABLE 23. CHEMICAL COST SUMMARY

1-Stage Activated Sludge To Achieve 0.025 mg/ℓ Total Cyanide		
Present cyanide effluent concentration, mg/ℓ	Required carbon dose, mg/ℓ	Chemical cost $/million gallons
0.05	36	106
0.10	108	286
2-Stage Activated Sludge To Achieve 0.025 mg/ℓ Total Cyanide		
Present cyanide effluent concentration, mg/ℓ	Required carbon dose, mg/ℓ	Chemical cost $/million gallons
0.05	9.4	40
0.10	28.0	86

Based upon 1 mg/ℓ $CuCl_2$ (as Cu^{+2}) and carbon cost of $.30/pound and $CuCl_2$ cost of $1.91/pound (as Cu^{+2}).

was prepared. Placement of granular activated sludge system (with $CuCl_2$ and oxygen addition), would bring this refinery into compliance with the Illinois effluent standard of 0.025 mg/ℓ. Based on pilot plant data and an effluent flow of 4.2 MGD, the refinery estimated 51,000 pounds per day of carbon would be exhausted. Assuming a carbon regeneration furnace is purchased and an attrition loss of 10%, fresh carbon make-up would be 5,100 pounds per day. Ignoring the large capital investment required for the granular carbon system, the chemical costs for both systems are compared in Table 24.

Even with the thermal regeneration of the granular carbon, the make-up carbon alone would cost $3,000 a day, as compared with $210 or $810 per day for the powdered carbon cost without any regeneration. Taking into consideration the differences in capital investment, the PAC system is even more advantageous.

To provide some indication of the range of operating costs expected, chemical expenditures for the other refineries described in Table 1 were calculated. The values of Table 25 are based on an effluent level of 0.025 mg/ℓ total cyanide and a copper concentration of 1.0 mg/ℓ. Depending upon the effluent characteristics of the refinery and the number of activated sludge stages, the costs varied from $20,000 to $530,000 per year. For any of the refineries listed in Table 25, the costs are much lower than the alternative cyanide treatment methods.

QUALITATIVE ECONOMIC ASPECTS

There are other aspects of the PAC/$CuCl_2$ system with offer economic advantanges that are more difficult to quantify. The following list of benefits from the addition of PAC into an activated sludge unit should reduce the operating costs assessed to cyanide removal even further:

1. The fluctuation in daily effluent cyanide levels is reduced, (except during periods of high organic loadings).
2. Although not observed in the laboratory activated sludge reactors, PAC is reported to lower effluent suspended solids.
3. Lower effluent BOD's are achieved.
4. Sludge dewatering characteristics are improved.

While PAC/$CuCl_2$ addition offers some economic advantages over other processes, this process is not without its drawbacks. Where effluent cyanide standards are based on daily maximums as opposed to monthly averages, the value of this system is reduced. As occurred in Test D, slug doses of high-strength organic wastes can result in a desorption of cyanide from the carbon, resulting in significantly higher effluent cyanide levels. Thus, where wide fluctuations in the organic loading exist, high cyanide effluent peaks will occur for one or more days. Where a two-stage sludge system is used, the organic fluctuations should be reduced.

TABLE 24. CYANIDE TREATMENT - CHEMICAL COST COMPARISON

System	Carbon cost, $/day	Copper cost, $/day	Total Chemical cost, $/day
Granular carbon - with thermal regeneration	3,000	67	3,067
Powdered carbon - no regeneration 1-stage activated sludge system[1]	810	67	877
Powdered carbon - no regeneration 2-stage activated sludge system[2]	210	67	277

Design Basis:

Flow 4.2 MGD
Existing cyanide effluent level - 0.079 mg/ℓ
Design cyanide effluent level - 0.025 mg/ℓ
Granular activated carbon - $0.60/lb
Powdered activated carbon - $0.30/lb
Cupric chloride - $1.91/lb (as Cu^{+2})

[1] Apparent cyanide loading 0.7 mg CN^-/gm carbon
[2] Apparent cyanide loading 2.7 mg CN^-/gm carbon

TABLE 25. COST ESTIMATES FOR PAC/$CuCl_2$ SYSTEM

Refinery	No. of stages in activated sludge	Effluent flow rate, MGD	Existing effluent cyanide, mg/ℓ	Annual operating costs, $
A	1	2.6	0.176	530,000
A	2	2.6	0.176	150,000
B	1	4.2	0.079	320,000
B	2	4.2	0.079	100,000
E	1	2.0	0.038	46,000
E	2	2.0	0.038	20,000
F	1	6.8	0.045	220,000
F	2	6.8	0.045	86,000

Design basis:

Cyanide effluent level - 0.025 mg/ℓ monthly average
PAC - \$.30/lb, $CuCl_2$ - \$1.91/lb (as Cu^{+2})
Apparent CN^- Loadings: 1-stage - 0.7 mg CN^-/gm carbon
2-stage - 2.7 mg CN^-/gm carbon

In summary, the PAC/$CuCl_2$ system has definite economic advantages over existing cyanide treatment methods available to the refining industry. This system is perhaps best suited for refineries requiring less than a 60% reduction in effluent cyanide levels and especially for refineries with two-stage activated sludge units. Because there is no capital expenditure required to utilize the PAC/$CuCl_2$ system, its use is extremely flexible. For example, some refineries experience high effluent cyanide levels for one to two months after bringing the catalytic cracking unit back into operation after a major maintenance shutdown. The PAC/$CuCl_2$ system is ideally suited for short-term use in such instances where high cyanide levels are projected. As discussed in Section 3, many refineries also experience one to three months each year of very high effluent cyanide levels. The PAC/$CuCl_2$ system provides an economic approach to reducing these cyanide levels. When the effluent cyanide levels are in compliance, no carbon or copper needs to be added. For refineries that require high degrees of cyanide reduction on a yearly basis, Table 25 provides an indication that over $500,000 per year of powdered carbon may be required. While not included in this economic evaluation, PAC regeneration by wet air oxidation would reduce the overall cost of treatment for the larger PAC users.

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APPENDIX

TABLE A-1. TABULATION OF ALL DATA FROM PHASE I.

Test & Reactor No.	6-hr CN^- Conc., mg/ℓ	Equilibrium CN^- Conc., mg/ℓ	Carbon Conc., mg/ℓ	Type of Carbon[1]	Initial Copper Conc., mg/ℓ	Initial CN^- Conc., mg/ℓ	Type of CN^-	Filtrate Copper Conc. at 6 hr, mg/ℓ	Used in Regression Analysis
1-1	< 0.01	< 0.01	250	H.D.	1.5	0.48	Ferro	1.8	No[2]
-2	0.027	0.024	250	H.D.	1.5	0.48	Ferro	0.05	Yes
-3	0.060	0.038	250	H.D.	1.5	0.53	Ferro	0.05	Yes
2-1	< 0.01	—	250	H.D.	1.5	0.44	Ferri	1.7	No[3]
-2	0.01	—	250	H.D.	1.5	0.50	Ferri	0.05	No[3]
-3	0.05	--	250	H.D.	1.5	0.52	Ferri	0.02	No[3]
3-1	0.30	0.28	250	H.D.	0.0	0.53	Ferro	< 0.02	Yes
-2	< 0.01	< 0.01	250	H.D.	1.5	0.52	Ferro	0.10	Yes
-3	< 0.01	0.013	250	H.D.	1.5	0.39	Ferro	0.10	Yes
4-1	0.168	0.120	250	H.D.	0.5	0.48	Ferro	0.05	Yes
-2	0.145	0.115	250	H.D.	0.5	0.37	Ferro	0.05	Yes
-3	0.010	< 0.01	250	H.D.	1.5	0.39	Ferro	0.15	Yes
5-1	< 0.01	< 0.01	250	H.D.	10.0	0.46	Ferro	0.4	No[4]
-2	0.040	0.025	250	H.D.	0.75	0.42	Ferro	0.05	Yes
-3	0.010	0.010	250	H.D.	1.0	0.46	Ferro	0.05	Yes
-4	0.010	< 0.01	250	H.D.	1.25	0.46	Ferro	0.05	Yes
6	Test aborted after six hours, reactor split open; repeated as Test 7.								
7-2	0.16	0.025	100	H.D.	1.0	0.34	Ferro	0.05	Yes
-3	0.12	--	250	H.D.	1.0	0.44	Ferro	0.05	No[5]
-4	0.05	0.13	1,000	H.D.	1.0	0.38	Ferro	< 0.02	No[6]
8-1	0.23	0.11	0	--	0.5	0.53	Ferro	0.12	No[7]
-2	0.46	0.39	100	L.D.	0.5	0.53	Ferro	0.08	Yes
-3	0.39	0.29	250	L.D.	0.5	0.66	Ferro	0.05	Yes
-4	0.023	0.023	1,000	L.D.	0.5	0.57	Ferro	< 0.02	Yes
9-2	0.29	0.12	100	L.D.	1.0	0.41	Ferro	0.12	Yes
-3	0.29	0.16	250	L.D.	1.0	0.67	Ferro	0.05	Yes
-4	0.015	0.01	1,000	L.D.	1.0	0.50	Ferro	0.02	Yes
10-1	—	0.41	0	--	0.0	0.67	Ferro	--	No[7]
-2	0.32	0.26	250	L.D.	1.5	0.69	Ferro	0.18	Yes
-3	0.50	0.45	100	H.D.	0.5	0.66	Ferro	0.04	No[8]
-4	0.26	0.27	100	H.D.	1.5	0.70	Ferro	0.19	No[8]
11-3	0.29	0.30	250	H.D.	1.0	0.63	Ferri	--	No[3]
-4	0.15	0.10	250	L.D.	1.0	0.67	Ferri	--	No[3]
12-3	--	0.09	100	H.D.	1.0	0.40	Ferro	--	No[8]
-4	—	0.24	100	H.D.	0.5	0.41	Ferro	--	No[8]
13-3	--	0.63	0	—	0.0	0.66	Ferro	< 0.02	No[9]
-4	—	0.51	0	--	0.5	0.65	Ferro	0.17	No[9]

[1] H.D. -- High Density, lignite-based; L.D. -- Low Density, lignin-based carbon.

[2] pH too low, did not have enough pH variation to analyze statistically.

[3] Ferricyanide data not used, too few tests.

[4] Copper dosage beyond concentration range.

[5] Lost equilibrium cyanide sample during analysis -- boiled over.

[6] Equilibrium value appears erroneous, does not agree with 6-hr cyanide sample.

[7] Suspect reactor contaminated with carbon particles.

[8] Final data collected after regression analysis completed.

[9] Without carbon in the system, any removal would be by a different mechanism.

APPENDIX

TABLE A-2. DATA FROM PHASE II TEST A - BASELINE OPERATION

	Cyanide Conc. mg/ℓ			BOD mg/ℓ			Total Organic Carbon mg/ℓ			Flow ℓ/day		Suspended Solids mg/ℓ			MLSS*** mg/ℓ		Copper Conc.** mg/ℓ		
Date	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2
2-19	0.23	0.059	0.065	310	15	9	--	--	--	19	24	--	--	--	--	--	--	--	--
20	--	--	--	130	14	10	89	22	28	24	17	--	14	5	2968	2805	--	--	--
21	--	--	--	340	7	14	--	--	--	11	14	--	--	--	--	--	--	--	--
22	--	--	--	--	--	--	--	--	--	12	13	--	30	52	2339	3013	--	--	--
23	0.19	0.067	0.012	120	9	5	91	37	31	165	22	--	<5	<5	2982	3159	--	--	--
24	--	--	--	--	--	--	--	--	--	21	16	--	--	--	--	--	--	--	--
25	0.21	0.020	0.020	280	19	19	106	26	27	18	14	--	31	28	2411	2717	--	--	--
26	--	--	--	340	19	22	--	--	--	15	22	--	--	--	--	--	--	--	--
27	0.15	0.018	0.012	270	21	14	84	27	25	15	19	--	24	23	2622	2377	--	--	--
28	--	--	--	360	16	16	--	--	--	5	--	--	--	--	--	--	--	--	--
29	0.11	0.004	0.008	--	--	--	--	--	--	14	11	--	--	--	--	--	--	--	--
3-1	--	--	--	156	12	3	66	23	19	11	14	--	25	10	2194	2126	--	--	--
2	0.13	0.002	0.008	--	--	--	--	--	--	11	12	--	--	--	--	--	--	--	--
3	0.14	0.002	0.006	293	9	8	90	25	20	16	14	41	8	3	1931	1870	--	--	--
4	0.13	0.006	0.004	242	6	10	--	--	--	17	21	--	--	--	--	--	--	--	--
5	0.13	0.004	0.002	168	9	10	79	22	22	19.5	18	--	16	10	1795	1981	--	--	--
6	0.24	0.001	0.001	219	19	23	--	--	--	18.5	19	--	--	--	--	--	--	--	--
7	0.15	0.008	0.004	--	--	--	--	--	--	18	14	--	--	--	--	--	--	--	--
8	0.21	0.002	0.014	127	11	11	100	26	26	8	13.5	--	8	10	1667	1792	--	--	--
9	0.20	0.018	0.026	--	--	--	--	--	--	23	22.5	--	--	--	--	--	--	--	--
10	0.19	0.010	0.012	130	8	9	97	23	23	23	22	27	9	7	1642	1646	--	--	--
Mean	0.17	0.016	0.014	250	13	14	111	27	31	16.0	16.7	25	22	21	2237	2369	--	--	--

* Both reactors operated without Copper or PAC addition

** Copepr not monitored during Test A

*** Sludge was wasted at a rate of 800 ml/day from each aeration basin

APPENDIX

TABLE A-3. DATA FROM PHASE II TEST B LOW CARBON/LOW COPPER*

	Cyanide Conc. mg/ℓ			COD mg/ℓ			Total Organic Carbon mg/ℓ			Flow ℓ/day		Suspended Solids mg/ℓ			MLSS** mg/ℓ		Copper Conc. mg/ℓ		
Date	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2
3-11	0.21	0.008	0.016	220	10	14	97	23	23	21.5	21.5	--	--	--	--	--	<.01	<.01	0.05
12	0.18	0.014	0.018	230	15	24	104	26	30	22.5	17.5	--	5	14	1861	1633	--	--	--
13	0.17	0.006	0.008	450	6	29	--	--	--	16	20	--	--	--	--	--	0.05	<.01	0.20
14	0.19	0.014	0.010	--	--	--	--	--	--	18	18	--	--	--	--	--	--	--	--
15	0.20	0.008	0.010	80	11	20	19	18	18	18	18	--	6	8	2020	1964	--	--	--
16	0.20	0.008	0.010	--	--	--	--	--	--	9	9	--	--	--	--	--	<.01	<.01	0.16
17	0.21	0.004	0.012	124	10	25	--	--	--	17	21	--	6	13	1117	1341	--	--	--
18	0.23	0.006	0.012	230	10	34	--	--	--	8	20.5	--	7	23	949	1207	<.01	<.01	0.18
19	0.021	0.012	0.010	510	52	60	430	29	36	19.5	19	--	9	37	1970	1296	--	--	--
20	0.027	0.008	0.012	160	16	20	--	--	--	18	17.5	--	--	--	--	--	<.01	<.01	0.15
21	0.048	0.026	0.020	--	--	--	--	--	--	17	18	--	--	--	--	--	--	--	--
22	0.42	0.028	0.037	210	17	22	156	33	21.5	17.5	17.5	--	24	13	1373	1499	--	--	--
23	0.33	0.022	0.024	--	--	--	--	--	--	16.5	16.5	--	--	--	--	--	<.02	<.02	0.20
24	0.45	0.014	0.032	190	19	48	109	21	26.5	18	17.5	--	6	2	1898	1719	--	--	--
25	0.37	0.020	0.022	--	--	--	--	--	--	19	17	--	--	--	--	--	--	--	--
26	0.43	0.040	0.028	150	14	35	138	21.5	24.5	20	22	--	4	15	2187	1835	--	<.02	0.12
27	0.41	0.032	0.024	750	21	36	--	--	--	22	20	--	--	--	--	--	--	--	--
28	0.40	0.020	0.037	--	--	--	--	--	--	21	19	--	--	--	--	--	--	--	--
29	0.35	0.028	0.030	210	16	24	112	31.5	21	21.5	20	--	8	8	1705	1871	<.02	<.02	0.17
Mean	0.31	0.017	0.020	280	16.5	30.0	145	24	25	17.9	18.4	--	8	15	--	--	<.02	<.02	0.15

* Reactor 1 is a control with no copper or PAC
Reactor 2 has 250 mg/day PAC and 0.5 mg/ℓ copper
Sludge age 12 days in both reactors

** Sludge wasted at a rate of 800 ml/day from both reactors

APPENDIX

TABLE A-4. DATA FROM PHASE II TEST C HIGH CARBON/LOW COPPER*

	Cyanide Conc. mg/ℓ			BOD mg/ℓ			Total Organic Carbon mg/ℓ			Flow ℓ/day		Suspended Solids mg/ℓ		MLSS** mg/ℓ		Copper Conc. mg/ℓ		
Date	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2
4-1	0.67	0.040	0.065	--	--	--	--	--	--	8	11	--	--	--	--	--	--	--
2	0.59	0.062	0.32	390	29	32	170	30	30	21	17	15	11	2030	2054	--	<.02	0.15
3	0.60	0.059	0.037	336	16	18	--	--	--	20	20	--	--	--	--	--	--	--
4	0.67	0.049	0.047	--	--	--	--	--	--	18	22	--	--	--	--	--	--	--
5	0.53	0.062	0.064	273	13	23	121	23	25	15.5	15.5	6	13	1349	2149	--	<.02	0.12
6	0.72	0.067	0.042	--	--	--	--	--	--	18.5	19	--	--	--	--	--	--	--
7	0.68	0.056	0.035	500	30	30	117	30	29	19	20	16	14	1957	2812	<.02	<.02	0.07
8	0.60	0.028	0.027	550	35	37	--	--	--	20.5	19.5	--	--	--	--	--	--	--
9	0.59	0.049	0.032	305	42	37	136	35	36	21	21	13	13	1639	2870	--	<.02	0.07
10	0.72	0.090	0.030	349	20	28	--	--	--	22	22	--	--	--	--	--	--	--
11	0.80	0.110	0.056	--	--	--	--	--	--	22	24	--	--	--	--	--	--	--
12	0.72	0.103	0.065	400	30	18	124	28	22	21	21	7	6	1663	2492	--	--	--
13	0.69	0.096	0.056	--	--	--	--	--	--	21.5	21.5	--	--	--	--	--	--	--
14	0.65	0.087	0.081	320	25	25	110	14	12	21.5	12.5	3	4	1924	3166	<.02	<.02	0.07
Mean	0.66	0.067	0.048	380	27	28	130	27	26	19.25	19.0	10	10	--	--	<.02	<.02	0.10

* Reactor 1 is a control with no Copepr or PAC added
Reactor 2 has 750 mg/day of PAC and 0.5 mg/ℓ copper added
Sludge Age 15 days in both reactors

** Sludge wasted at a rate of 650 mℓ/day from both reactors

APPENDIX

TABLE A-5. DATA FROM PHASE II TEST D HIGH CARBON/HIGH COPPER*

	Cyanide Conc. mg/ℓ			BOD mg/ℓ			Total Organic Carbon mg/ℓ			Flow ℓ/day		Suspended Solids		MLSS** mg/ℓ		Copper Conc. mg/ℓ		
Date	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Inlet	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Effluent 1	Effluent 2	Reactor 1	Reactor 2	Inlet	Effluent 1	Effluent 2
Period 1																		
4-16	0.74	0.052	0.026	310	14	20	120	25	24.5	21.5	21	6	4	2019	3234	--	<.02	0.08
17	0.74	0.049	0.030	440	22	15	--	--	--	21.5	21	--	--	--	--	--	--	--
18	0.54	0.044	0.024	--	--	--	--	--	--	21	19.5	--	--	--	--	--	--	--
19	0.53	0.052	0.035	230	29	12	106	25.5	20.5	22	19	6	5	1619	3160	--	<.02	0.12
20	0.53	0.032	0.022	--	--	--	--	--	--	14.5	15.5	--	--	--	--	--	--	--
21	0.53	0.065	0.030	310	18	30	--	--	--	19	21	7	5	2231	3312	<.02	<.02	0.14
22	0.57	0.106	0.044	210	30	32	--	--	--	18.5	21.5	--	--	--	--	--	--	--
23	0.54	0.084	0.049	230	45	30	86.6	25	29.5	18.5	20.5	7	4	1621	3065	--	--	--
24	0.49	0.067	0.049	240	19	37	--	--	--	19	22	--	--	--	--	--	--	--
25	0.67	0.070	0.049	--	--	--	--	--	--	18	19.5	--	--	--	--	--	--	--
26	0.53	0.084	0.065	--	--	--	99	24	21	19	20.5	21	8	2051	3126	--	<.02	0.14
27	0.49	0.087	0.059	--	--	--	--	--	--	21.5	21	--	--	--	--	--	--	--
28	0.56	0.078	0.062	--	--	--	--	--	--	21.5	20.5	9	7	2027	2979	--	--	--
29	0.85	0.096	0.065	--	--	--	--	--	--	20.5	21.5	--	--	--	--	--	--	--
30	0.67	0.096	0.084	380	83	97	117	16	19.5	19.5	21.5	13	28	1368	1593	--	<.02	0.18
5-1	0.72	0.100	0.049	400	44	33	--	--	--	20	20	--	--	--	--	--	--	*--
Mean	0.61	0.073	0.045	330	34	34	106	24	23	19.7	20.3	99	9	--	--	<.02	<.02	0.13
Period 2																		
5-2	0.57	0.090	0.127	--	--	--	--	--	--	17	18	--	--	--	--	--	--	--
3	0.41	0.110	0.202	420	30	31	74	27	32	17	16	12	16	1738	1201	--	<.02	0.28
4	0.54	0.096	0.135	--	--	--	--	--	--	16	16	--	--	--	--	--	--	--
5	0.50	0.100	0.120	220	46	4	104	31	36	18	17	9	9	991	900	<.02	<.02	0.26
6	0.54	0.170	0.110	240	51	8	--	--	--	15.5	16.5	--	--	--	--	--	--	--
7	0.47	0.180	0.140	180	34	12	137	23	40	18	17	10	26	705	996	--	<.02	0.29
8	0.34	0.103	0.103	320	60	21	130	31.5	38	20	19	--	--	--	--	--	--	--
9	0.53	0.110	0.140	--	--	--	--	--	--	18	19	--	--	--	--	--	--	--
10	--	--	--	--	--	--	134	20	39	17.5	18	9	32	1560	2325	--	<.02	0.28
11	0.53	0.127	0.191	--	--	--	--	--	--	16.5	18	--	--	--	--	--	--	--
12	0.67	0.120	0.127	330	24	9	127.5	28	37	18	18	10	29	1390	2597	<.02	<.02	0.28
13	0.67	0.100	0.123	280	14	12	--	--	--	17.5	16.5	--	--	--	--	--	--	--
14	0.70	0.135	0.160	140	40	18	283.5	34.5	46	19.5	20	13	24	1110	1784	--	<.02	0.28
15	0.70	0.140	0.144	320	16	17	--	--	--	21	20	--	--	--	--	--	--	--
16	0.70	0.148	0.127	--	--	--	--	--	--	18	18	--	--	--	--	--	--	--
Mean	0.56	0.114	0.139	272	37	15	141	28	38	17.8	17.7	10.5	22.3	--	--	<.02	<.02	0.28
Period 3																		
5-17	0.70	0.175	0.103	--	--	--	--	--	--	18	20	10	7	1780	2740	<.02	--	0.16
18	0.45	0.151	0.072	--	--	--	--	--	--	19.5	22	--	--	--	--	--	--	--
19	--	--	--	100	55	56	71.5	14.5	17.5	23.5	25	10	10	761	1180	<.02	<.02	0.15
20	0.51	0.084	0.032	270	35	66	--	--	--	21.5	22	--	--	--	--	--	--	--
21	0.51	0.116	0.042	300	60	39	70.1	14.1	12.4	22	21	10	9	1246	1960	<.02	<.02	0.18
22	0.54	0.093	0.047	--	--	--	--	--	--	23.5	23	--	--	--	--	--	--	--
23	0.54	0.106	0.093	--	--	--	--	--	--	23	18.5	--	--	--	--	--	--	--
24	0.32	0.100	0.084	--	--	--	124	17.8	21	22	22	11	5	1797	1378	--	<.02	0.19
25	0.40	0.191	0.135	--	--	--	--	--	--	20	19	--	--	--	--	--	--	--
26	0.40	0.115	0.155	--	--	--	47.4	19.2	19.3	24	24	11	12	1707	1651	<.02	<.02	0.20
27	0.45	0.078	0.090	230	18	15	--	--	--	22	21	--	--	--	--	--	--	--
28	0.45	0.096	0.186	182	75	22	58	31	31	18	16	11	27	1172	2376	<.02	<.02	0.23
Mean	0.50	0.120	0.094	216	48.6	39.6	74.2	19.3	20.2	21.4	21.1	10.5	11.7	--	--	<.02	<.02	0.19

* Reactor 1 is a control unit with no Copper or PAC added
Reactor 2 has 250 mg/day PAC and 1.0 mg/ℓ of copper added.
Sludge Age was 15 days during the first 2 periods and was reduced to 10 days for the final period.

** Sludge was wasted at a rate of 650 mℓ/day from both aeration basins during the first 2 periods and at a rate of 1000 mℓ/day for the final period

APPENDIX

TABLE A-6. DATA FROM PHASE II TEST E TWO STAGE TEST, MEDIUM CARBON/HIGH COPPER*

	Cyanide Conc. mg/ℓ			BOD mg/ℓ			Total Organic Carbon mg/ℓ			Flow ℓ/day		Suspended Solids mg/ℓ		MLSS** mg/ℓ		Copper Conc. mg/ℓ		
Date	Inlet	Effluent 3	Effluent 4	Inlet	Effluent 3	Effluent 4	Inlet	Effluent 3	Effluent 4	Reactor 3	Reactor 4	Effluent 3	Effluent 4	Reactor 3	Reactor 4	Inlet	Effluent 3	Effluent 4
5-30	0.087	0.087	0.197	--	--	--	--	--	--	17	10	--	--	--	--	--	--	--
31	--	--	--	--	--	--	13	10	11	20	21	5	4.6	636	205	<.02	0.21	<.02
6-01	--	--	--	--	--	--	--	--	--	20	21	--	--	--	--	<.02	--	--
2	0.090	0.044	0.227	--	--	--	20	6	7	18	20	10	3.4	1156	243	<.02	0.11	<.02
3	0.180	0.100	0.148	150	19	70	42	10	10	20	21	--	--	--	--	<.02	0.20	<.02
4	0.180	0.103	0.151	88	27	36	40	10	11	19	21	4	5.4	494	238	<.02	0.23	<.02
5	0.113	0.062	0.127	62	17	28	--	--	--	20	21	--	--	--	--	--	--	--
6	0.180	0.062	0.170	--	--	--	--	--	--	18	21	--	--	--	--	--	--	--
7	0.081	0.044	0.191	47	13	17	17	12	14	22	21	4	5.4	646	214	<.02	0.19	<.02
8	0.130	0.032	0.040	41	8	10	--	--	--	22	22	--	--	--	--	--	--	--
9	0.155	0.056	0.070	97	18	14	19	12	10	22	22	6	5	835	424	<.02	0.11	<.02
10	0.202	0.065	0.087	89	43	13	--	--	--	22	22	--	--	--	--	--	--	--
11	--	--	--	--	--	--	24	13	12	--	--	6	6	790	402	--	0.35	<.02
Mean	0.140	0.066	0.141	82	21	27	25	10	11	20	20	5.8	5.0	--	--	<.02	0.20	<.02

*Reactor 4 is a control unit with no copper or PAC added
Reactor 3 has 500 mg/day PAC and 1.0 mg/ℓ of copper added
Sludge age was 15 days

**Sludge was wasted at a rate of 650 mℓ/day from both aeration basins

APPENDIX

TABLE A-7. BATCH TEST CYANIDE DECAY DATA

Test and Reactor No.	mg of CN^- per gram of Carbon at:								
	Initial	0.01 days	1 day	2 days	3 days	4 days	5 days	6 days	7 days
1-1	1.83	--	1.77	1.01	--	--	1.37	--	--
1-2	1.81	--	1.71	1.33	--	--	0.84	--	--
1-3	2.02	--	1.99	1.67	--	--	1.17	--	--
3-1	2.20	--	1.45	1.33	1.49	1.43	--	--	--
3-2	1.99	1.91	1.80	1.77	1.76	1.69	--	--	--
4-1	1.81	1.72	1.58	1.68	1.63	1.76	--	--	1.58
4-2	1.70	--	1.57	1.57	1.47	1.64	--	--	--
4-3	1.78	--	1.74	1.74	1.64	1.65	--	--	1.28
7-2	3.74	--	--	2.95	--	2.84	--	--	--
7-4	0.53	--	--	0.45	--	0.39	--	--	--
9-2	5.29	--	3.86	4.10	--	4.01	--	3.16	--
9-3	2.56	2.38	2.12	2.25	--	1.98	--	1.60	--
9-4	0.67	--	0.58	0.56	--	0.50	--	0.58	--

GLOSSARY

acclimation: Period during which the microogranisms become accustomed to their new environment and substrate.

activated sludge process: A method of secondary wastewater treatment in which a mixture of wastewater and activated sludge is agitated and aerated. The activated sludge is subsequently separated from the treated wastewater (mixed liquor) by sedimentation, and wasted or returned to the process as needed.

aeration: The bringing about of intimate contact between air and liquid by one of the following methods: spraying the liquid in the air, bubbling air through the liquid, or agitation of the liquid to promote surface absorption of air.

apparent loading: The amount of soluble organic material (as measured by any suitable test such as TOC) removed by a Powdered Activated Carbon (PAC) system, less the amount of removed by a biological system at the same sludge age divided by the applied carbon dosage.

$$\text{Apparent Loading} = \frac{\Delta\text{Organics (PAC)} - \Delta\text{Organics (BIO)}}{\text{Applied Carbon Dosage}}$$

average daily flow: The average quantity of wastewater passing through the system in a 24 hour period.

biochemical oxygen demand (BOD): A measure of the oxygen necessary to satisfy the requirements for the aerobic decomposition of the decomposable organic matter ina liquid by bacteria, The standard (BOD_5) is five days at 20°C.

biological fouling: A decrease in the real loading on the Powdered Activated Carbon (PAC) as a result of micro-organisms and their by-products on the carbon surface.

biological seed: Sludge which is mixed with composed wastewater for the purpose of introducing acclimated organisms, thereby accelerating the initial stages of biological growth and the decomposition of organics in the wastewater.

chemical oxygen demand (COD): A measure of the oxygen required to approach total oxidation of the organic matter in the waste.

clarifier: A tank or basin, in which wastewater is retained for a sufficient time, and in which the velocity of flow is sufficiently low to remove by gravity a part of the suspended matter.

coefficient of determination (R^2): Statistical device used to measure the "goodness of fit" of the regression analysis defined by the following equation:

$$R^2 = \frac{\text{regression sum of squares}}{\text{total sum of squares}} = \frac{\Sigma(\hat{Y}_i - \bar{y})^2}{\Sigma(Y_i - \bar{y})^2}$$

where:

Y_i = observed y

$\hat{Y}_i$ = y calculated from regression coefficients

$\bar{y}$ = mean value of observed y

completely mixed activate sludge: Treatment system in which the untreated wastewater is instantly mixed through the entire aeration basin.

composite sample: Integrated sample collected as a portion of the total flow.

complex cyanides: Compounds containing the cyanide group, CN^-, in combination with other elements forming a complex radical, such as ferricyanide and ferrocyanide, $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$, respectively.

$CuCl_2$: Cupric chloride.

cyanides: Compounds containing the CN^- group, in both the simple and/or complex modes, unless otherwise noted.

detention time: Period of time required for a liquid to flow through a tank or unit.

dissolved oxygen (DO): Free or uncombined oxygen in a liquid.

effluent: Liquid flowing out of the treatment system.

filtrate: Liquid passing through a filtering medium with a specified pore size.

floc: Small gelatinous masses, formed in water or wastewater by biochemical processes, or by agglomeration.

flocculation: The bringing together of flocculating particles by hydraulic or mechanical means.

influent: Liquid flowing into a basin or treatment plant.

mean: Average value of all observations defined $\bar{x} = \frac{\Sigma x_i}{n}$

n = number of observations
x_i = value of "ith" observation

milligrams per liter (mg/ℓ): The weight of material in one liter of liquid.

mixed liquor (ML): A mixture of sludge and wastewater in a biological reaction tank undergoing biological degradation in an activated sludge system.

nutrient: Any substance absorbed by organisms which promotes growth and replacement of cellular parts, such a phosphorous.

PAC: Powdered activated carbon.

pH: The negative logarithim of the hydrogen ion concentration. It is used to express the intensity of the acid or alkaline condition of a solution.

settleable solids: Suspended solids which will settle in sedimentation basins (clarifiers) in normal detention times.

simple cyanides: Cyanide that may be determined by the Wood River modified Roberts-Jackson procedure. This procedure measures the amount of free cyanide as HCN, which includes readily hydrolyzed metal cyanide complexes such as nickel and copper cyanides. Cyanides not included are bound in complex form, such as ferricyanide, and ferrocyanide.

sludge: The accumulated settled solids separated from wastewater in clarifiers, and containing more or less water to form a semi-liquid mass.

sludge age: The average total time of detention of a suspended solids particle in a system. It is defined as the total weight of suspended solids in the aeration basin divided by the total weight of suspended solids in the effluent and otherwise wasted per day.

sludge volume index (SVI): The volume of sludge occupied by one gram of activated sludge after 30 minutes of quiescent settling in a 1,000 ml graduated cylinder.

standard deviation(s): Measure of the deviation of the x's form the sample mean. The square root of the variance, which measures the dispersion of the distribution.

For paired observations the sample standard deviation is:

$$s = \sqrt{\frac{\Sigma(x_1 - x_2)^2}{n} - (\text{mean difference})^2}$$

Then the unbiased standard deviation is:

$$\sigma = \frac{s}{\sqrt{n-1}}$$

substrate: Raw waste feed on which a microorganism grows or is placed to grow by decomposing the waste material.

substrate removal: The total BOD in plant influent, minus the soluble BOD in plant effluent, divided by the total influent BOD.

supernatant liquor: The liquid overlying settled solids.

suspended solids (SS or TSS): The quantity of material deposited when a quantity of wastewater is filtered through an asbestos mat in a Gooch crucible or equal method.

t-test: To test a hypothesis assuming a normally distributed variable in the t-distribution can be used to determine the probability level of occurrence. It is defined as follows:

$$T_{n-1} = \frac{(\bar{x}-\mu_0)}{s} \; \overline{n}$$

where:

$\bar{x}$ = mean sample value
μ_0 = true mean hypothesized
n = number of observations
$n-1$ = degrees of freedom
s = standard deviation

total organic carbon (TOC): The amount of carbon, measured as C, in the form of organic compounds, dissolved in an aqueous solution.

total solids (TS): The solids in the wastewater, both suspended and dissolved.

volatile suspended solids (VSS): The quantity of suspended solids in wastewater that are lost on ignition of the total suspended solids.

waste sludge: Sludge which is no longer needed in the treatment system and therefore is removed and disposed of.